

4. Industrial Processes

Greenhouse gas emissions are produced as a by-product of various non-energy-related industrial activities. That is, these emissions are produced from an industrial process itself and are not directly a result of energy consumed during the process. For example, raw materials can be chemically transformed from one state to another. This transformation can result in the release of greenhouse gases such as carbon dioxide (CO₂), methane (CH₄), or nitrous oxide (N₂O). The processes addressed in this chapter include iron and steel production, cement manufacture, ammonia manufacture and urea application, lime manufacture, limestone and dolomite use (e.g., flux stone, flue gas desulfurization, and glass manufacturing), soda ash manufacture and use, titanium dioxide production, phosphoric acid production, ferroalloy production, CO₂ consumption, aluminum production, petrochemical production, silicon carbide production and consumption, lead production, zinc production, nitric acid production, and adipic acid production (see Figure 4-1).

Figure 4-1: 2005 Industrial Processes Chapter Greenhouse Gas Sources

In addition to the three greenhouse gases listed above, there are also industrial sources of man-made fluorinated compounds called hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆). The present contribution of these gases to the radiative forcing effect of all anthropogenic greenhouse gases is small; however, because of their extremely long lifetimes, many of them will continue to accumulate in the atmosphere as long as emissions continue. In addition, many of these gases have high global warming potentials; SF₆ is the most potent greenhouse gas the Intergovernmental Panel on Climate Change (IPCC) has evaluated. Usage of HFCs for the substitution of ozone depleting substances is growing rapidly, as they are the primary substitutes for ozone depleting substances (ODSs), which are being phased-out under the *Montreal Protocol on Substances that Deplete the Ozone Layer*. In addition to their use as ODS substitutes, HFCs, PFCs, SF₆, and other fluorinated compounds are employed and emitted by a number of other industrial sources in the United States. These industries include aluminum production, HCFC-22 production, semiconductor manufacture, electric power transmission and distribution, and magnesium metal production and processing.

In 2005, industrial processes generated emissions of 333.8 teragrams of CO₂ equivalent (Tg CO₂ Eq.), or 5 percent of total U.S. greenhouse gas emissions. CO₂ emissions from all industrial processes were 147.0 Tg CO₂ Eq. (147,026 Gg) in 2005, or 2 percent of total U.S. CO₂ emissions. CH₄ emissions from industrial processes resulted in emissions of approximately 2.0 Tg CO₂ Eq. (97 Gg) in 2005, which was less than 1 percent of U.S. CH₄ emissions. N₂O emissions from adipic acid and nitric acid production were 21.7 Tg CO₂ Eq. (70 Gg) in 2005, or 5 percent of total U.S. N₂O emissions. In 2005, combined emissions of HFCs, PFCs and SF₆ totaled 163.0 Tg CO₂ Eq. Overall, emissions from industrial processes increased by 11.2 percent from 1990 to 2005 despite decreases in emissions from several industrial processes, such as iron and steel, aluminum production, ammonia manufacture and urea application, HCFC-22 production, and electrical transmission and distribution. The increase in overall emissions was driven by a rise in the emissions originating from cement manufacture and, primarily, the emissions from the use of substitutes for ozone depleting substances.

Table 4-1 summarizes emissions for the Industrial Processes chapter in units of Tg CO₂ Eq., while unweighted native gas emissions in gigagrams (Gg) are provided in Table 4-2.

Table 4-1: Emissions from Industrial Processes (Tg CO₂ Eq.)

Gas/Source	1990	1995	2000	2001	2002	2003	2004	2005
CO₂	175.6	171.9	166.9	152.9	152.1	148.9	153.0	147.0
Cement Manufacture	33.3	36.8	41.2	41.4	42.9	43.1	45.6	45.9
Iron and Steel Production	85.0	73.5	65.3	58.0	54.7	53.5	51.5	45.4
Ammonia Manufacture & Urea Application	19.3	20.5	19.6	16.7	17.8	16.2	16.9	16.3
Lime Manufacture	11.3	12.8	13.3	12.9	12.3	13.0	13.7	13.7

Limestone and Dolomite Use	5.5	7.4	6.0	5.7	5.9	4.7	6.7	7.4
Soda Ash Manufacture and Consumption	4.1	4.3	4.2	4.1	4.1	4.1	4.2	4.2
Aluminum Production	6.8	5.7	6.1	4.4	4.5	4.5	4.2	4.2
Petrochemical Production	2.2	2.8	3.0	2.8	2.9	2.8	2.9	2.9
Titanium Dioxide Production	1.3	1.7	1.9	1.9	2.0	2.0	2.3	1.9
Ferroalloy Production	2.2	2.0	1.9	1.5	1.3	1.3	1.4	1.4
Phosphoric Acid Production	1.5	1.5	1.4	1.3	1.3	1.4	1.4	1.4
CO ₂ Consumption	1.4	1.4	1.4	0.8	1.0	1.3	1.2	1.3
Zinc Production	0.9	1.0	1.1	1.0	0.9	0.5	0.5	0.5
Lead Production	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Silicon Carbide Production and Consumption	0.4	0.3	0.2	0.2	0.2	0.2	0.2	0.2
CH₄	2.2	2.4	2.5	2.2	2.1	2.1	2.2	2.0
Petrochemical Production	0.9	1.1	1.2	1.1	1.1	1.1	1.2	1.1
Iron and Steel Production	1.3	1.3	1.2	1.1	1.0	1.0	1.0	1.0
Ferroalloy Production	+	+	+	+	+	+	+	+
Silicon Carbide Production and Consumption	+	+	+	+	+	+	+	+
N₂O	33.0	37.1	25.6	20.8	23.1	22.9	21.8	21.7
Nitric Acid Production	17.8	19.9	19.6	15.9	17.2	16.7	16.0	15.7
Adipic Acid Production	15.2	17.2	6.0	4.9	5.9	6.2	5.7	6.0
HFCs, PFCs, and SF₆	89.3	103.5	143.8	133.8	143.0	142.7	153.9	163.0
Substitution of Ozone Depleting Substances	0.3	32.2	80.9	88.6	96.9	105.5	114.5	123.3
HCFC-22 Production ^a	35.0	27.0	29.8	19.8	19.8	12.3	15.6	16.5
Electrical Transmission and Distribution ^b	27.1	21.8	15.2	15.1	14.3	13.8	13.6	13.2
Semiconductor Manufacture	2.9	5.0	6.3	4.5	4.4	4.3	4.7	4.3
Aluminum Production	18.5	11.8	8.6	3.5	5.2	3.8	2.8	3.0
Magnesium Production and Processing ^b	5.4	5.6	3.0	2.4	2.4	2.9	2.6	2.7
Total	300.2	314.9	338.8	309.7	320.3	316.6	330.8	333.8

1 + Does not exceed 0.05 Tg CO₂ Eq.

2 ^a HFC-23 emitted

3 ^b SF₆ emitted

4 Note: Totals may not sum due to independent rounding.

6 Table 4-2: Emissions from Industrial Processes (Gg)

Gas/Source	1990	1995	2000	2001	2002	2003	2004	2005
CO₂	175,621	171,943	166,937	152,904	152,130	148,903	152,977	147,026
Cement Manufacture	33,278	36,847	41,190	41,357	42,898	43,082	45,603	45,910
Iron and Steel Production	85,034	73,454	65,259	58,047	54,702	53,511	51,492	45,440
Ammonia Manufacture & Urea Application	19,306	20,453	19,616	16,719	17,766	16,173	16,894	16,321
Lime Manufacture	11,273	12,844	13,344	12,861	12,330	13,022	13,728	13,660
Limestone and Dolomite Use	5,533	7,359	5,960	5,733	5,885	4,720	6,702	7,397
Soda Ash Manufacture and Consumption	4,141	4,304	4,181	4,147	4,139	4,111	4,205	4,228
Aluminum Production	6,831	5,659	6,086	4,381	4,490	4,503	4,231	4,208
Petrochemical Production	2,221	2,750	3,004	2,787	2,857	2,777	2,895	2,897
Titanium Dioxide Production	1,308	1,670	1,918	1,857	1,997	2,013	2,259	1,921
Ferroalloy Production	2,152	2,036	1,893	1,459	1,349	1,305	1,419	1,392
Phosphoric Acid Production	1,529	1,513	1,382	1,264	1,338	1,382	1,395	1,383
CO ₂ Consumption	1,415	1,423	1,416	825	978	1,310	1,199	1,324
Zinc Production	939	1,003	1,129	976	927	502	472	460
Lead Production	285	298	311	293	290	289	259	265
Silicon Carbide Production and Consumption	375	329	248	199	183	202	224	219
CH₄	106	116	117	103	101	101	106	97
Petrochemical Production	41	52	58	51	52	51	55	51

Iron and Steel Production	63	62	57	51	48	49	50	45
Ferroalloy Production	1	1	1	+	+	+	+	+
Silicon Carbide Production and Consumption	1	1	1	+	+	+	+	+
N₂O	107	120	83	67	75	74	70	70
Nitric Acid Production	58	64	63	51	56	54	52	51
Adipic Acid Production	49	56	19	16	19	20	19	19
HFCs, PFCs, and SF₆	M	M	M	M	M	M	M	M
Substitution of Ozone Depleting Substances	M	M	M	M	M	M	M	M
HCFC-22 Production ^a	3	2	3	2	2	1	1	1
Electrical Transmission and Distribution ^b	1	1	1	1	1	1	1	1
Semiconductor Manufacture	M	M	M	M	M	M	M	M
Aluminum Production	M	M	M	M	M	M	M	M
Magnesium Production and Processing ^b	+	+	+	+	+	+	+	+
NO_x	591	607	626	656	532	533	534	535
CO	4,125	3,959	2,217	2,339	1,710	1,730	1,751	1,772
NMVOCs	2,422	2,642	1,773	1,769	1,811	1,813	1,815	1,818

+ Does not exceed 0.5 Gg

M (Mixture of gases)

^a HFC-23 emitted

^b SF₆ emitted

Note: Totals may not sum due to independent rounding.

In order to ensure the quality of the emission estimates from industrial processes, Tier 1 quality assurance and quality control (QA/QC) procedures and checks have been performed on all industrial process sources. Where performed, Tier 2 procedures focused on the emission factor and activity data sources and methodology used for estimating emissions, and will be described within the QA/QC and Verification Discussion of that source description. In addition to the national QA/QC plan, a more detailed plan was developed specifically for the CO₂ and CH₄ industrial processes sources. This plan was based on the U.S. strategy, but was tailored to include specific procedures recommended for these sources.

The general method employed to estimate emissions for industrial processes, as recommended by the IPCC, involves multiplying production data (or activity data) for each process by an emission factor per unit of production. The uncertainty in the emission estimates is therefore generally a function of a combination of the uncertainties surrounding the production and emission factor variables. Uncertainty of activity data and the associated probability density functions for industrial processes CO₂ sources were estimated based on expert assessment of available qualitative and quantitative information. Uncertainty estimates and probability density functions for the emission factors used to calculate emissions from this source were devised based on IPCC recommendations.

Activity data is obtained through a survey of manufacturers conducted by various organizations (specified within each source); the uncertainty of the activity data is a function of the reliability of plant-level production data and is influenced by the completeness of the survey response. The emission factors used were either derived using calculations that assume precise and efficient chemical reactions, or were based upon empirical data in published references. As a result, uncertainties in the emission coefficients can be attributed to, among other things, inefficiencies in the chemical reactions associated with each production process or to the use of empirically-derived emission factors that are biased; therefore, they may not represent U.S. national averages. Additional assumptions are described within each source.

The uncertainty analysis performed to quantify uncertainties associated with the 2005 inventory estimates from industrial processes continues a multi-year process for developing credible quantitative uncertainty estimates for these source categories using the IPCC Tier 2 approach. As the process continues, the type and the characteristics of the actual probability density functions underlying the input variables are identified and better characterized

(resulting in development of more reliable inputs for the model, including accurate characterization of correlation between variables), based primarily on expert judgment. Accordingly, the quantitative uncertainty estimates reported in this section should be considered illustrative and as iterations of ongoing efforts to produce accurate uncertainty estimates. The correlation among data used for estimating emissions for different sources can influence the uncertainty analysis of each individual source. While the uncertainty analysis recognizes very significant connections among sources, a more comprehensive approach that accounts for all linkages will be identified as the uncertainty analysis moves forward.

4.1. Cement Manufacture (IPCC Source Category 2A1)

Cement manufacture is an energy- and raw-material-intensive process that results in the generation of CO₂ from both the energy consumed in making the cement and the chemical process itself.¹ Cement production, at the most recent estimation, accounted for about 2.4 percent of total global industrial and energy-related CO₂ emissions (IPCC 1996, USGS 2003). Cement is manufactured in 37 states and Puerto Rico. CO₂ emitted from the chemical process of cement production is the largest source of industrial CO₂ emissions in the United States.

During the cement production process, calcium carbonate (CaCO₃) is heated in a cement kiln at a temperature of about 1,300°C (2,400°F) to form lime (i.e., calcium oxide or CaO) and CO₂ in a process known as calcination or calcining. A very small amount of carbonates other than CaCO₃ is also present in the raw material; however, for calculation purposes all of the raw material is assumed to be CaCO₃. Next, the lime is combined with silica-containing materials to produce clinker (an intermediate product), with the earlier by-product CO₂ being released to the atmosphere. The clinker is then allowed to cool, mixed with a small amount of gypsum, and used to make Portland cement. Additional CO₂ emissions result from the production of masonry cement, which accounts for approximately 6 percent of total clinker production, and is produced using lime and Portland cement. However, this additional lime is already accounted for in the Lime Manufacture source category in this chapter; therefore, the additional emissions from making masonry cement from clinker are not counted in this source category's total. They are presented here for informational purposes only.

In 2005, U.S. clinker production—including Puerto Rico—totaled 88,783 thousand metric tons (Van Oss 2006). The resulting emissions of CO₂ from 2005 cement production were estimated to be 45.9 Tg CO₂ Eq. (45,910 Gg) (see Table 4-3). Emissions from masonry production from clinker raw material are accounted for under Lime Manufacture.

Table 4-3: CO₂ Emissions from Cement Production (Tg CO₂ Eq. and Gg)*

Year	Tg CO ₂ Eq.	Gg
1990	33.3	33,278
1995	36.8	36,847
2000	41.2	41,190
2001	41.4	41,357
2002	42.9	42,898
2003	43.1	43,082
2004	45.6	45,603
2005	45.9	45,910

* Totals exclude CO₂ emissions from making masonry cement from clinker, which are accounted for under Lime Manufacture.

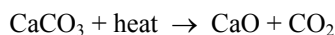
After falling in 1991 by two percent from 1990 levels, cement production emissions have grown every year since.

¹ The CO₂ emissions related to the consumption of energy for cement manufacture are accounted for under CO₂ from Fossil Fuel Combustion in the Energy chapter.

Overall, from 1990 to 2005, emissions increased by 38 percent. Cement continues to be a critical component of the construction industry; therefore, the availability of public construction funding, as well as overall economic growth, have had considerable influence on cement production.

Methodology

CO₂ emissions from cement manufacture are created by the chemical reaction of carbon-containing minerals (i.e., calcining limestone). While in the kiln, limestone is broken down into CO₂ and lime with the CO₂ released to the atmosphere. The quantity of CO₂ emitted during cement production is directly proportional to the lime content of the clinker. During calcination, each mole of CaCO₃ (i.e., limestone) heated in the clinker kiln forms one mole of lime (CaO) and one mole of CO₂:



CO₂ emissions were estimated by applying an emission factor, in tons of CO₂ released per ton of clinker produced, to the total amount of clinker produced. The emission factor used in this analysis is the product of the average lime fraction for clinker of 64.6 percent (IPCC 2000) and a constant reflecting the mass of CO₂ released per unit of lime. This calculation yields an emission factor of 0.507 tons of CO₂ per ton of clinker produced, which was determined as follows:

$$EF_{\text{Clinker}} = 0.646 \text{ CaO} \times \left[\frac{44.01 \text{ g/mole CO}_2}{56.08 \text{ g/mole CaO}} \right] = 0.507 \text{ tons CO}_2/\text{ton clinker}$$

During clinker production, some of the clinker precursor materials remain in the kiln as non-calcinated, partially calcinated, or fully calcinated cement kiln dust (CKD). The emissions attributable to the calcinated portion of the CKD are not accounted for by the clinker emission factor. The IPCC recommends that these additional CKD CO₂ emissions should be estimated as two percent of the CO₂ emissions calculated from clinker production. Total cement production emissions were calculated by adding the emissions from clinker production to the emissions assigned to CKD (IPCC 2000).

Masonry cement requires additional lime over and above the lime used in clinker production. In particular, non-plasticizer additives such as lime, slag, and shale are added to the cement, increasing its weight by approximately five percent. Lime accounts for approximately 60 percent of this added weight. Thus, the additional lime is equivalent to roughly 2.86 percent of the starting amount of the product, since:

$$0.6 \times 0.05 / (1 + 0.05) = 2.86\%$$

An emission factor for this added lime can then be calculated by multiplying this 2.86 percent by the molecular weight ratio of CO₂ to CaO (0.785) to yield 0.0224 metric tons of additional CO₂ emitted for every metric ton of masonry cement produced.

As previously mentioned, the CO₂ emissions from the additional lime added during masonry cement production are accounted for in the section on CO₂ emissions from Lime Manufacture. Thus, the activity data for masonry cement production are shown in this chapter for informational purposes only, and are not included in the cement emission totals.

The 1990 through 2005 activity data for clinker and masonry cement production (see Table 4-4) were obtained through a personal communication with Hendrick Van Oss (Van Oss 2006) of the USGS and through the USGS *Mineral Yearbook: Cement* (USGS 1993 through 2005). The data were compiled by USGS through questionnaires sent to domestic clinker and cement manufacturing plants.

Table 4-4: Cement Production (Gg)

Year	Clinker	Masonry
------	---------	---------

1990	64,355	3,209
1995	71,257	3,603
2000	79,656	4,332
2001	79,979	4,450
2002	82,959	4,449
2003	83,315	4,737
2004	88,190	5,000
2005	88,783	5,514

Uncertainty

The uncertainties contained in these estimates are primarily due to uncertainties in the lime content of clinker and in the percentage of CKD recycled inside the clinker kiln. Uncertainty is also associated with the amount of lime added to masonry cement, but it is accounted for under the Lime Manufacture source category. The lime content of clinker varies from 64 to 66 percent. CKD loss can range from 1.5 to 8 percent depending upon plant specifications. Additionally, some amount of CO₂ is reabsorbed when the cement is used for construction. As cement reacts with water, alkaline substances such as calcium hydroxide are formed. During this curing process, these compounds may react with CO₂ in the atmosphere to create calcium carbonate. This reaction only occurs in roughly the outer 0.2 inches of surface area. Because the amount of CO₂ reabsorbed is thought to be minimal, it was not estimated.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-5. Cement Manufacture CO₂ emissions were estimated to be between 40.0 and 52.0 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 13 percent below and 13 percent above the emission estimate of 45.9 Tg CO₂ Eq.

Table 4-5: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Cement Manufacture (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Cement Manufacture	CO ₂	45.9	40.0	52.0	-13%	+13%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

The historical activity data used to calculate the emissions from cement production were updated for the year 2004. The change resulted in a decrease of 0.04 Tg CO₂ Eq. (less than one percent) in CO₂ emissions from cement production for that year.

4.2. Iron and Steel Production (IPCC Source Category 2C1)

In addition to being an energy intensive process, the production of iron and steel also generates process-related emissions of CO₂ and CH₄. Iron is produced by first reducing iron oxide (iron ore) with metallurgical coke in a blast furnace to produce pig iron (impure iron containing about 3 to 5 percent C by weight). Metallurgical coke is manufactured using coking coal as a raw material. Iron may be introduced into the blast furnace in the form of raw iron ore, pellets, briquettes, or sinter. Pig iron is used as a raw material in the production of steel, which contains about 0.4 percent C by weight. Pig iron is also used as a raw material in the production of iron products in foundries. The pig iron production process produces CO₂ emissions and fugitive CH₄ emissions.

The production of metallurgical coke from coking coal and the consumption of the metallurgical coke used as a reducing agent in the blast furnace are considered in the inventory to be non-energy (industrial) processes, not energy (combustion) processes. Metallurgical coke is produced by heating coking coal in a coke oven in a low-oxygen environment. The process drives off the volatile components of the coking coal and produces coal (metallurgical) coke. Coke oven gas and coal tar are C containing by-products of the coke manufacturing process. Coke oven gas is generally burned as a fuel within the steel mill. Coal tar is used as a raw material to produce anodes used for primary aluminum production and other electrolytic processes, and also used in the production of other coal tar products. The coke production process produces CO₂ emissions and fugitive CH₄ emissions.

Sintering is a thermal process by which fine iron-bearing particles, such as air emission control system dust, are baked, which causes the material to agglomerate into roughly one-inch pellets that are then recharged into the blast furnace for pig iron production. Iron ore particles may also be formed into larger pellets or briquettes by mechanical means, and then agglomerated by heating prior to being charged into the blast furnace. The sintering process produces CO₂ emissions and fugitive CH₄ emissions.

The metallurgical coke is a reducing agent in the blast furnace. CO₂ is produced as the metallurgical coke used in the blast furnace process is oxidized and the iron is reduced. Steel is produced from pig iron in a variety of specialized steel-making furnaces. The majority of CO₂ emissions from the iron and steel process come from the use of coke in the production of pig iron, with smaller amounts evolving from the removal of C from pig iron used to produce steel. Some C is also stored in the finished iron and steel products.

Emissions of CO₂ and CH₄ from iron and steel production in 2005 were 45.4 Tg CO₂ Eq. (45,440 Gg) and 1.0 Tg CO₂ Eq. (45 Gg), respectively (see Table 4-6 and Table 4-7), totaling 46.4 Tg CO₂ Eq. Emissions have fluctuated significantly from 1990 to 2005 due to changes in domestic economic conditions and changes in product imports and exports. In 2005, domestic production of pig iron decreased by 12.0 percent and coal coke production decreased by 1.1 percent. Overall, domestic pig iron and coke production have declined since the 1990s. Pig iron production in 2005 was 21 percent lower than in 2000 and 24 percent below 1990 levels. Coke production in 2005 was 20 percent lower than in 2000 and 39 percent below 1990 levels. Overall, emissions from iron and steel productions have declined by 47% (40.0 Tg CO₂ Eq.) from 1990 to 2005.

Table 4-6: CO₂ and CH₄ Emissions from Iron and Steel Production (Tg CO₂ Eq.)

Year	1990	1995	2000	2001	2002	2003	2004	2005
CO ₂	85.0	73.5	65.3	58.0	54.7	53.5	51.5	45.4
CH ₄	1.3	1.3	1.2	1.1	1.0	1.0	1.0	1.0
Total	86.4	74.8	66.5	59.1	55.7	54.5	52.5	46.4

Table 4-7: CO₂ and CH₄ Emissions from Iron and Steel Production (Gg)

Year	1990	1995	2000	2001	2002	2003	2004	2005
CO ₂	85,034	73,454	65,259	58,047	54,702	53,511	51,492	45,440
CH ₄	63	62	57	51	48	49	50	45

Methodology

Coking coal is used to manufacture metallurgical (coal) coke that is used primarily as a reducing agent in the production of iron and steel, but is also used in the production of other metals including lead and zinc (see Lead Production and Zinc Production in this chapter). The total coking coal consumed at coke plants and the total amount of coking coal produced were identified. These data were used to estimate the emissions associated with producing coke from coking coal and attributed to the production of iron and steel. Additionally, the amount of coke consumed to produce pig iron and the emissions associated with this production were estimated. The C content of the coking coal and coke consumed in these processes were estimated by multiplying the energy consumption by material specific C-content coefficients. The C content coefficients used are presented in Annex 2.1.

Emissions from the re-use of scrap steel were also estimated by assuming that all the associated C content of the

scrap steel, which has an associated C content of approximately 0.4 percent, are released during the scrap re-use process.

Lastly, emissions from C anodes, used during the production of steel in electric arc furnaces (EAFs), were also estimated. Emissions of CO₂ were calculated by multiplying the annual production of steel in EAFs by an emission factor (4.4 kg CO₂/ton steel_{EAF}). It was assumed that the C anodes used in the production of steel in EAFs are composed of 80 percent petroleum coke and 20 percent coal tar pitch (DOE 1997). Since coal tar pitch is a by-product of the coke production process and its C-related emissions have already been accounted for earlier in the iron and steel emissions calculation as part of the process, the emissions were reduced by the amount of C in the coal tar pitch used in the anodes to avoid double counting.

Emissions associated with the production of coke from coking coal, pig iron production, the re-use of scrap steel, and the consumption of C anodes during the production of steel were summed.

Additionally, the coal tar pitch component of C anodes consumed during the production of aluminum are accounted for in the aluminum production section of this chapter. The emissions were reduced by the amount of coal tar pitch used in aluminum production to avoid double counting. The amount of coal tar pitch consumed for processes other than the aluminum production and as EAF anodes and net imports of coal tar were also estimated. A storage factor was applied to estimate emissions associated with other coal tar pitch consumption and net imports.

C storage was accounted for by assuming that all domestically manufactured steel had a C content of 0.4 percent. Furthermore, any pig iron that was not consumed during steel production, but fabricated into finished iron products, was assumed to have a C content of 4 percent.

The potential CO₂ emissions associated with C contained in pig iron used for purposes other than iron and steel production, stored in the steel product, stored as coal tar, and attributed to C anode consumption during aluminum production were summed and subtracted from the total emissions estimated above.

The production processes for coal coke, sinter, and pig iron result in fugitive emissions of CH₄, which are emitted via leaks in the production equipment rather than through the emission stacks or vents of the production plants. The fugitive emissions were calculated by applying emission factors taken from the 1995 IPCC Guidelines (IPCC/UNEP/OECD/IEA 1995) (see Table 4-8) to annual domestic production data for coal coke, sinter, and pig iron.

Table 4-8: CH₄ Emission Factors for Coal Coke, Sinter, and Pig Iron Production (g/kg)

Material Produced	g CH₄/kg produced
Coal Coke	0.5
Pig Iron	0.9
Sinter	0.5

Source: IPCC/UNEP/OECD/IEA 1997.

Data relating to the amount of coal consumed at coke plants, and for the production of coke for domestic consumption in blast furnaces, were taken from the Energy Information Administration (EIA), Quarterly Coal Report October through December (EIA 1998, 1999, 2000, 2001, 2002, 2003, 2004a) and January through March (EIA 2006c). Data on total coke consumed for pig iron production were taken from the American Iron and Steel Institute (AISI), *Annual Statistical Report* (AISI 2001, 2002, 2003, 2004, 2005, 2006). Scrap steel consumption data for 1990 through 2005 were obtained from *Annual Statistical Report* (AISI 1995, 2001, 2002, 2003, 2004, 2005, 2006) (see Table 4-9). Crude steel production, as well as pig iron use for purposes other than steel production, was also obtained from *Annual Statistical Report* (AISI 1996, 2001, 2002, 2004, 2005, 2006). C content percentages for pig iron and crude steel and the CO₂ emission factor for C anode emissions from steel production were obtained from IPCC *Good Practice Guidance* (IPCC 2000). Data on the non-energy use of coking coal were obtained from EIA's *Emissions of U.S. Greenhouse Gases in the United States* (EIA 2004b, 2006b). Information on coal tar net imports was determined using data from the U.S. Bureau of the Census's U.S. International Trade Commission's Trade Dataweb (U.S. Bureau of the Census 2006). Coal tar consumption for

aluminum production data was estimated based on information gathered by EPA's Voluntary Aluminum Industrial Partnership (VAIP) program and data from USAA Primary Aluminum Statistics (USAA 2005, 2005, 2006) (see Aluminum Production in this chapter). Annual consumption of iron ore used in sinter production for 1990 through 2004 was obtained from the USGS *Iron Ore Yearbook* (USGS 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004) and for 2005 from the USGS Commodity Specialist (Jorgenson 2006). The CO₂ emission factor for C anode emissions from aluminum production was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Estimates for the composition of C anodes used during EAF steel and aluminum production were obtained from *Energy and Environmental Profile of the U.S. Aluminum Industry* (DOE 1997).

Table 4-9: Production and Consumption Data for the Calculation of CO₂ and CH₄ Emissions from Iron and Steel Production (Thousand Metric Tons)

Gas/Activity Data	1990	1995	2000	2001	2002	2003	2004	2005
CO₂								
Coal Consumption at Coke Plants	35,269	29,948	26,254	23,655	21,461	21,998	21,473	21,259
Coke Consumption for Pig Iron	25,043	22,288	19,307	17,236	15,959	15,482	15,068	13,848
Basic Oxygen Furnace Steel Production	56,216	56,721	53,965	47,359	45,463	45,874	47,714	42,705
Electric Arc Furnace Steel Production	33,510	38,472	47,860	42,774	46,125	47,804	51,969	52,194
CH₄								
Coke Production	25,054	21,545	18,877	17,191	15,221	15,579	15,340	15,167
Iron Ore Consumption for Sinter	12,239	12,575	10,784	9,234	9,018	8,984	8,047	8,313
Domestic Pig Iron Production for Steel	49,062	50,233	47,400	41,741	39,601	40,487	42,292	37,222

Uncertainty

The time series data sources for production of coal coke, sinter, pig iron, steel, and aluminum upon which the calculations are based are assumed to be consistent for the entire time series. The estimates of CO₂ emissions from the production and utilization of coke are based on consumption data, average C contents, and the fraction of C oxidized. Uncertainty is associated with the total U.S. coke consumption and coke consumed for pig iron production. These data are provided by different data sources (EIA and AISI) and comparisons between the two datasets for net imports, production, and consumption identified discrepancies; however, the data chosen are considered the best available. These data and factors produce a relatively accurate estimate of CO₂ emissions. However, there are uncertainties associated with each of these factors. For example, C oxidation factors may vary depending on inefficiencies in the combustion process, where varying degrees of ash or soot can remain unoxidized.

Simplifying assumptions were made concerning the composition of C anodes and the C contents of all pig iron and crude steel. It was also assumed that all coal tar used during anode production originates as a by-product of the domestic coking process. There is also uncertainty associated with the total amount of coal tar products produced and with the storage factor for coal tar. Uncertainty surrounding the CO₂ emission factor for C anode consumption in aluminum production was also estimated.

For the purposes of the CH₄ calculation it is assumed that none of the CH₄ is captured in stacks or vents and that all of the CH₄ escapes as fugitive emissions. Additionally, the CO₂ emissions calculation is not corrected by subtracting the C content of the CH₄, which means there may be a slight double counting of C as both CO₂ and CH₄.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-10. Iron and Steel CO₂ emissions were estimated to be between 40.8 and 57.4 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 10 percent below and 26 percent above the emission estimate of 45.4 Tg CO₂ Eq. Iron and Steel CH₄ emissions were estimated to be between 0.9 Tg CO₂ Eq. and 1.0 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 8 percent below and 8 percent above the emission estimate of 1.0 Tg CO₂ Eq.

Table 4-10: Tier 2 Quantitative Uncertainty Estimates for CO₂ and CH₄ Emissions from Iron and Steel Production (Tg. CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Iron and Steel Production	CO ₂	45.4	40.8	57.4	-10%	+26%
Iron and Steel Production	CH ₄	1.0	0.9	1.0	-8%	+8%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

CO₂ emission estimates for the iron and steel source category were updated for the entire time series to reflect revisions to the coal tar import/export data. These revisions resulted in a change in emissions of less than one percent throughout the time series.

Planned Improvements

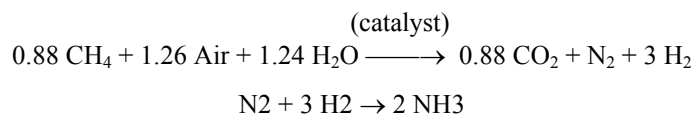
The methodology to estimate emissions from the Iron and Steel source category will be updated in future inventories to include methodologies outlined in the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006). These methodologies involve the inclusion of energy-related emissions in the iron and steel emission estimates as well as emissions associated with metallurgical coke production, sinter production, pellet production, and direct reduced iron production in addition to iron and steel production.

4.3. Ammonia Manufacture and Urea Application (IPCC Source Category 2B1)

Emissions of CO₂ occur during the production of synthetic ammonia, primarily through the use of natural gas as a feedstock. The natural gas-based, naphtha-based, and petroleum coke-based processes produce CO₂ and hydrogen (H₂), the latter of which is used in the production of ammonia. One nitrogen production plant located in Kansas is producing ammonia from petroleum coke feedstock. In some plants the CO₂ produced is captured and used to produce urea. The brine electrolysis process for production of ammonia does not lead to process-based CO₂ emissions.

There are five principal process steps in synthetic ammonia production from natural gas feedstock. The primary reforming step converts CH₄ to CO₂, carbon monoxide (CO), and H₂ in the presence of a catalyst. Only 30 to 40 percent of the CH₄ feedstock to the primary reformer is converted to CO and CO₂. The secondary reforming step converts the remaining CH₄ feedstock to CO and CO₂. The CO in the process gas from the secondary reforming step (representing approximately 15 percent of the process gas) is converted to CO₂ in the presence of a catalyst, water, and air in the shift conversion step. CO₂ is removed from the process gas by the shift conversion process, and the hydrogen gas is combined with the nitrogen (N₂) gas in the process gas during the ammonia synthesis step to produce ammonia. The CO₂ is included in a waste gas stream with other process impurities and is absorbed by a scrubber solution. In regenerating the scrubber solution, CO₂ is released.

The conversion process for conventional steam reforming of CH₄, including primary and secondary reforming and the shift conversion processes, is approximately as follows:



To produce synthetic ammonia from petroleum coke, the petroleum coke is gasified and converted to CO₂ and H₂. These gases are separated, and the H₂ is used as a feedstock to the ammonia production process, where it is reacted

with N₂ to form ammonia.

Not all of the CO₂ produced in the production of ammonia is emitted directly to the atmosphere. Both ammonia and CO₂ are used as raw materials in the production of urea [CO(NH₂)₂], which is another type of nitrogenous fertilizer that contains C as well as N. The chemical reaction that produces urea is:



The C in the urea that is produced and assumed to be subsequently applied to agricultural land as a nitrogenous fertilizer is ultimately released into the environment as CO₂; therefore, the CO₂ produced by ammonia production and subsequently used in the production of urea does not change overall CO₂ emissions. However, the CO₂ emissions are allocated to the ammonia and urea production processes in accordance to the amount of ammonia and urea produced.

Net emissions of CO₂ from ammonia manufacture in 2005 were 9.2 Tg CO₂ Eq. (9,197 Gg), and are summarized in Table 4-11 and Table 4-12. Emissions of CO₂ from urea application in 2005 totaled 7.1 Tg CO₂ Eq. (7,124 Gg), and are summarized in Table 4-11 and Table 4-12.

Table 4-11: CO₂ Emissions from Ammonia Manufacture and Urea Application (Tg CO₂ Eq.)

Source	1990	1995	2000	2001	2002	2003	2004	2005
Ammonia Manufacture	12.6	13.5	12.1	9.3	10.5	8.8	9.6	9.2
Urea Application	6.8	6.9	7.5	7.4	7.3	7.4	7.3	7.1
Total	19.3	20.5	19.6	16.7	17.8	16.2	16.9	16.3

Note: Totals may not sum due to independent rounding.

Table 4-12: CO₂ Emissions from Ammonia Manufacture and Urea Application (Gg)

Source	1990	1995	2000	2001	2002	2003	2004	2005
Ammonia Manufacture	12,553	13,546	12,128	9,321	10,501	8,815	9,571	9,197
Urea Application	6,753	6,907	7,488	7,398	7,266	7,358	7,323	7,124
Total	19,306	20,453	19,616	16,719	17,766	16,173	16,894	16,321

Note: Totals may not sum due to independent rounding.

Methodology

The calculation methodology for non-combustion CO₂ emissions from production of nitrogenous fertilizers from natural gas feedstock is based on a CO₂ emission factor published by the European Fertilizer Manufacturers Association (EFMA). The CO₂ emission factor (1.2 metric tons CO₂/metric ton NH₃) is applied to the percent of total annual domestic ammonia production from natural gas feedstock. Emissions of CO₂ from ammonia production are then adjusted to account for the use of some of the CO₂ produced from ammonia production as a raw material in the production of urea. For each ton of urea produced, 8.8 of every 12 tons of CO₂ are consumed and 6.8 of every 12 tons of ammonia are consumed. The CO₂ emissions reported for ammonia production are therefore reduced by a factor of 0.73 multiplied by total annual domestic urea production, and that amount of CO₂ emissions is allocated to urea fertilizer application. Total CO₂ emissions resulting from nitrogenous fertilizer production do not change as a result of this calculation, but some of the CO₂ emissions are attributed to ammonia production and some of the CO₂ emissions are attributed to urea application.

The calculation of the total non-combustion CO₂ emissions from nitrogenous fertilizers accounts for CO₂ emissions from the application of imported and domestically produced urea. For each ton of imported urea applied, 0.73 tons of CO₂ are emitted to the atmosphere. The amount of imported urea applied is calculated based on the net of urea imports and exports.

All ammonia production and subsequent urea production are assumed to be from the same process—conventional catalytic reforming of natural gas feedstock, with the exception of ammonia production from petroleum coke feedstock at one plant located in Kansas. The CO₂ emission factor for production of ammonia from petroleum coke is based on plant specific data, wherein all C contained in the petroleum coke feedstock that is not used for urea

production is assumed to be emitted to the atmosphere as CO₂ (Bark 2004). Ammonia and urea are assumed to be manufactured in the same manufacturing complex, as both the raw materials needed for urea production are produced by the ammonia production process. The CO₂ emission factor (3.57 metric tons CO₂/metric ton NH₃) is applied to the percent of total annual domestic ammonia production from petroleum coke feedstock.

The emission factor of 1.2 metric ton CO₂/metric ton NH₃ for production of ammonia from natural gas feedstock was taken from the EFMA Best Available Techniques publication, *Production of Ammonia* (EFMA 1995). The EFMA reported an emission factor range of 1.15 to 1.30 metric ton CO₂/metric ton NH₃, with 1.2 metric ton CO₂/metric ton NH₃ as a typical value. The EFMA reference also indicates that more than 99 percent of the CH₄ feedstock to the catalytic reforming process is ultimately converted to CO₂. The emission factor of 3.57 metric ton CO₂/metric ton NH₃ for production of ammonia from petroleum coke feedstock was developed from plant-specific ammonia production data and petroleum coke feedstock utilization data for the ammonia plant located in Kansas (Bark 2004). Ammonia and urea production data (see Table 4-13) were obtained from Coffeyville Resources (Coffeyville 2005, 2006) and the Census Bureau of the U.S. Department of Commerce (U.S. Census Bureau 1991, 1992, 1993, 1994, 1998, 1999, 2000, 2001a, 2001b, 2002a, 2002b, 2002c, 2003, 2004, 2005, 2006) as reported in *Current Industrial Reports Fertilizer Materials and Related Products* annual and quarterly reports. Import and export data for urea were obtained from the U.S. Census Bureau *Current Industrial Reports Fertilizer Materials and Related Products* annual and quarterly reports for 1997 through 2005 (U.S. Census Bureau 1998, 1999, 2000, 2001a, 2001b, 2002a, 2002b, 2002c, 2003, 2004, 2005, 2006), The Fertilizer Institute (TFI 2002) for 1993 through 1996, and the United States International Trade Commission Interactive Tariff and Trade DataWeb (U.S. ITC 2002) for 1990 through 1992 (see Table 4-13).

Table 4-13: Ammonia Production, Urea Production, and Urea Net Imports (Gg)

Year	Ammonia Production	Urea Production	Urea Net Imports
1990	15,425	8,124	1,086
1995	15,788	7,363	2,055
2000	14,342	6,969	3,241
2001	11,092	6,080	4,008
2002	12,577	7,038	2,870
2003	10,279	5,783	4,250
2004	10,939	5,755	4,230
2005	10,143	5,268	4,447

Uncertainty

The uncertainties presented in this section are primarily due to how accurately the emission factor used represents an average across all ammonia plants using natural gas feedstock. Uncertainties are also associated with natural gas feedstock consumption data for the U.S. ammonia industry as a whole, the assumption that all ammonia production and subsequent urea production was from the same process—conventional catalytic reforming of natural gas feedstock, with the exception of one ammonia production plant located in Kansas that is manufacturing ammonia from petroleum coke feedstock, and the assumption that 100 percent of the urea production and net imports are used as fertilizer or in otherwise emissive uses. It is also assumed that ammonia and urea are produced at collocated plants from the same natural gas raw material.

Such recovery may or may not affect the overall estimate of CO₂ emissions depending upon the end use to which the recovered CO₂ is applied. Further research is required to determine whether byproduct CO₂ is being recovered from other ammonia production plants for application to end uses that are not accounted for elsewhere.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-14. Ammonia Manufacture and Urea Application CO₂ emissions were estimated to be between 15.0 and 17.6 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 8 percent below and 8 percent above the emission estimate of 16.3 Tg CO₂ Eq.

Table 4-14: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Ammonia Manufacture and Urea Application (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ammonia Manufacture and Urea Application	CO ₂	16.3	15.0	17.6	-8%	+8%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

Estimates of CO₂ emissions from ammonia manufacture and urea application for the years 2002 and 2003 were revised to reflect updated data from the U.S. Census Bureau Current Industrial Report. These changes resulted in a decrease in CO₂ emissions from urea manufacture of 0.7 Tg CO₂ Eq. (10 percent) for 2002 and an increase of 0.9 Tg CO₂ Eq. (13 percent) for 2003.

Planned Improvements

Future improvements to the ammonia-manufacture and urea-application source category include updating emission factors to include both fuel and feedstock CO₂ emissions and incorporating CO₂ capture and storage if U.S. plants are found to use CO₂ capture technology. Methodologies will also be updated if additional ammonia-production plants are found to use hydrocarbons other than natural gas for ammonia production.

4.4. Lime Manufacture (IPCC Source Category 2A2)

Lime is an important manufactured product with many industrial, chemical, and environmental applications. Its major uses are in steel making, flue gas desulfurization (FGD) systems at coal-fired electric power plants, construction, and water purification. Lime has historically ranked fifth in total production of all chemicals in the United States. For U.S. operations, the term “lime” actually refers to a variety of chemical compounds. These include calcium oxide (CaO), or high-calcium quicklime; calcium hydroxide (Ca(OH)₂), or hydrated lime; dolomitic quicklime ([CaO•MgO]); and dolomitic hydrate ([Ca(OH)₂•MgO] or [Ca(OH)₂•Mg(OH)₂]).

Lime production involves three main processes: stone preparation, calcination, and hydration. CO₂ is generated during the calcination stage, when limestone—mostly calcium carbonate (CaCO₃)—is roasted at high temperatures in a kiln to produce CaO and CO₂. The CO₂ is given off as a gas and is normally emitted to the atmosphere. Some of the CO₂ generated during the production process, however, is recovered at some facilities for use in sugar refining and precipitated calcium carbonate (PCC)² production. It is also important to note that, for certain applications, lime reabsorbs CO₂ during use (see Uncertainty, below).

Lime production in the United States—including Puerto Rico—was reported to be 19,984 thousand metric tons in 2005 (USGS 2006). This resulted in estimated CO₂ emissions of 13.7 Tg CO₂ Eq. (or 13,660 Gg) (see Table 4-15 and Table 4-16).

Table 4-15: Net CO₂ Emissions from Lime Manufacture (Tg CO₂ Eq.)

Year	Tg CO ₂ Eq.
1990	11.3

² Precipitated calcium carbonate is a specialty filler used in premium-quality coated and uncoated papers.

1995	12.8
2000	13.3
2001	12.9
2002	12.3
2003	13.0
2004	13.7
2005	13.7

Table 4-16: CO₂ Emissions from Lime Manufacture (Gg)

Year	Potential	Recovered*	Net Emissions
1990	11,766	(493)	11,273
1995	13,741	(896)	12,844
2000	14,577	(1,233)	13,344
2001	13,978	(1,118)	12,861
2002	13,381	(1,051)	12,330
2003	14,171	(1,149)	13,022
2004	14,853	(1,125)	13,728
2005	14,831	(1,171)	13,660

* For sugar refining and precipitated calcium carbonate production.

Note: Totals may not sum due to independent rounding. Parentheses indicate negative values.

The contemporary lime market is distributed across five end-use categories as follows: metallurgical uses, 36 percent; environmental uses, 28 percent; chemical and industrial uses, 21 percent; construction uses, 14 percent; and refractory dolomite, 1 percent. In the construction sector, hydrated lime is still used to improve durability in plaster, stucco, and mortars. In 2005, the amount of hydrated lime used for traditional building increased slightly from 2004 levels to 493 metric tons (USGS 2006).

Lime production in 2005 slightly increased over 2004, the third annual increase in production after four years of decline. Overall, from 1990 to 2005, lime production has increased by 26 percent. The increase in production is attributed in part to growth in demand for environmental applications, especially flue gas desulfurization technologies. In 1993, EPA completed regulations under the Clean Air Act capping sulfur dioxide (SO₂) emissions from electric utilities. Lime scrubbers' high efficiencies and increasing affordability have allowed the flue gas desulfurization end-use to expand significantly over the years. Phase II of the Clean Air Act Amendments, which went into effect on January 1, 2000, remains the driving force behind the growth in the flue gas desulfurization market (USGS 2003).

Methodology

During the calcination stage of lime manufacture, CO₂ is given off as a gas and normally exits the system with the stack gas. To calculate emissions, the amounts of high-calcium and dolomitic lime produced were multiplied by their respective emission factors. The emission factor is the product of a constant reflecting the mass of CO₂ released per unit of lime and the average calcium plus magnesium oxide (CaO + MgO) content for lime (95 percent for both types of lime). The emission factors were calculated as follows:

For high-calcium lime:

$$[(44.01 \text{ g/mole CO}_2) \div (56.08 \text{ g/mole CaO})] \times (0.95 \text{ CaO/lime}) = 0.75 \text{ g CO}_2/\text{g lime}$$

For dolomitic lime:

$$[(88.02 \text{ g/mole CO}_2) \div (96.39 \text{ g/mole CaO})] \times (0.95 \text{ CaO/lime}) = 0.87 \text{ g CO}_2/\text{g lime}$$

Production was adjusted to remove the mass of chemically combined water found in hydrated lime, using the midpoint of default ranges provided by the IPCC *Good Practice Guidance* (IPCC 2000). These factors set the chemically combined water content to 24.3 percent for high-calcium hydrated lime, and 27.3 percent for dolomitic hydrated lime.

Lime production in the United States was 19,984 thousand metric tons in 2005 (USGS 2006), resulting in potential CO₂ emissions of 14.8 Tg CO₂ Eq. Some of the CO₂ generated during the production process, however, was recovered for use in sugar refining and PCC production. Combined lime manufacture by these producers was 1,964 thousand metric tons in 2005. It was assumed that approximately 80 percent of the CO₂ involved in sugar refining and PCC was recovered, resulting in actual CO₂ emissions of 13.7 Tg CO₂ Eq.

Lime production data (high-calcium- and dolomitic-quicklime, high-calcium- and dolomitic-hydrated, and dead-burned dolomite) for 1990 through 2005 (see Table 4-17) were obtained from USGS (1992 through 2005). Natural hydraulic lime, which is produced from CaO and hydraulic calcium silicates, is not produced in the United States (USGS 2005). Total lime production was adjusted to account for the water content of hydrated lime and is presented with lime consumption by sugar refining and PCC production in Table 4-18 (USGS 1992 through 2005). The CaO and CaO•MgO contents of lime were obtained from the IPCC *Good Practice Guidance* (IPCC 2000). Since data for the individual lime types (high calcium and dolomitic) was not provided prior to 1997, total lime production for 1990 through 1996 was calculated according to the three year distribution from 1997 to 1999. For sugar refining and PCC, it was assumed that 100 percent of lime manufacture and consumption was high-calcium, based on communication with the National Lime Association (Males 2003).

Table 4-17: High-Calcium- and Dolomitic-Quicklime, High-Calcium- and Dolomitic-Hydrated, and Dead-Burned-Dolomite Lime Production (Gg)

Year	High-Calcium Quicklime	Dolomitic Quicklime	High-Calcium Hydrated	Dolomitic Hydrated	Dead-Burned Dolomite
1990	11,166	2,234	1,781	319	342
1995	13,165	2,635	2,027	363	308
2000	14,300	3,000	1,550	421	200
2001	13,600	2,580	2,030	447	200
2002	13,400	2,420	1,500	431	200
2003	13,900	2,460	2,140	464	200
2004	14,200	3,020	2,140	421	200
2005	14,100	2,990	2,220	474	200

Table 4-18: Adjusted Lime Production and Lime Use for Sugar Refining and PCC (Gg)

Year	High-Calcium	Dolomitic	Use for Sugar Refining and PCC
1990	12,514	2,809	826
1995	14,700	3,207	1,503
2000	15,473	3,506	2,067
2001	15,137	3,105	1,874
2002	14,536	2,934	1,762
2003	15,520	2,998	1,926
2004	15,820	3,526	1,887
2005	15,781	3,535	1,964

Uncertainty

The uncertainties contained in these estimates can be attributed to slight differences in the chemical composition of these products. Although the methodology accounts for various formulations of lime, it does not account for the trace impurities found in lime, such as iron oxide, alumina, and silica. Due to differences in the limestone used as a raw material, a rigid specification of lime material is impossible. As a result, few plants manufacture lime with exactly the same properties.

In addition, a portion of the CO₂ emitted during lime manufacture will actually be reabsorbed when the lime is consumed. As noted above, lime has many different chemical, industrial, environmental, and construction applications. In many processes, CO₂ reacts with the lime to create calcium carbonate (e.g., water softening). CO₂ reabsorption rates vary, however, depending on the application. For example, 100 percent of the lime used to produce precipitated calcium carbonate reacts with CO₂; whereas most of the lime used in steel making reacts with impurities such as silica, sulfur, and aluminum compounds. A detailed accounting of lime use in the United States and further research into the associated processes are required to quantify the amount of CO₂ that is reabsorbed.³

In some cases, lime is generated from calcium carbonate by-products at pulp mills and water treatment plants.⁴ The lime generated by these processes is not included in the USGS data for commercial lime consumption. In the pulping industry, mostly using the Kraft (sulfate) pulping process, lime is consumed in order to causticize a process liquor (green liquor) composed of sodium carbonate and sodium sulfide. The green liquor results from the dilution of the smelt created by combustion of the black liquor where biogenic C is present from the wood. Kraft mills recover the calcium carbonate “mud” after the causticizing operation and calcine it back into lime—thereby generating CO₂—for reuse in the pulping process. Although this re-generation of lime could be considered a lime manufacturing process, the CO₂ emitted during this process is mostly biogenic in origin, and therefore is not included in Inventory totals.⁵

In the case of water treatment plants, lime is used in the softening process. Some large water treatment plants may recover their waste calcium carbonate and calcine it into quicklime for reuse in the softening process. Further research is necessary to determine the degree to which lime recycling is practiced by water treatment plants in the United States.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-19. Lime CO₂ emissions were estimated to be between 12.6 and 14.8 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 8 percent below and 8 percent above the emission estimate of 13.7 Tg CO₂ Eq.

Table 4-19: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Lime Manufacture (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound

³ Representatives of the National Lime Association estimate that CO₂ reabsorption that occurs from the use of lime may offset as much as a quarter of the CO₂ emissions from calcination (Males 2003).

⁴ Some carbide producers may also regenerate lime from their calcium hydroxide by-products, which does not result in emissions of CO₂. In making calcium carbide, quicklime is mixed with coke and heated in electric furnaces. The regeneration of lime in this process is done using a waste calcium hydroxide (hydrated lime) [CaC₂ + 2H₂O → C₂H₂ + Ca(OH)₂], not calcium carbonate [CaCO₃]. Thus, the calcium hydroxide is heated in the kiln to simply expel the water [Ca(OH)₂ + heat → CaO + H₂O] and no CO₂ is released.

⁵ Based on comments submitted by and personal communication with Dr. Sergio F. Galeano, Geortia-Pacific Corporation.

Lime Manufacture	CO ₂	13.7	12.6	14.8	-8%	+8%
------------------	-----------------	------	------	------	-----	-----

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

Corrections were made to the chemically combined water content percentages of high-calcium hydrated lime and dolomitic hydrated lime. This change resulted in a 0.2 percent increase in emissions on average throughout the time series. Estimates of CO₂ from lime manufacture for the year 2004 were revised to reflect updated data from the USGS. These changes resulted in a decrease in CO₂ emissions from lime manufacture of less than one percent for 2004.

Planned Improvements

Future inventories are anticipated to include emissions associated with lime kiln dust (LKD) in the lime emission estimates. Research will be conducted to determine the availability of LKD data in the United States for inclusion in the emission estimates.

4.5. Limestone and Dolomite Use (IPCC Source Category 2A3)

Limestone (CaCO₃) and dolomite (CaCO₃MgCO₃)⁶ are basic raw materials used by a wide variety of industries, including construction, agriculture, chemical, metallurgy, glass manufacture, and environmental pollution control. Limestone is widely distributed throughout the world in deposits of varying sizes and degrees of purity. Large deposits of limestone occur in nearly every state in the United States, and significant quantities are extracted for industrial applications. For some of these applications, limestone is sufficiently heated during the process and generates CO₂ as a by-product. Examples of such applications include limestone used as a flux or purifier in metallurgical furnaces, as a sorbent in flue gas desulfurization systems for utility and industrial plants, or as a raw material in glass manufacturing and magnesium production.

In 2005, approximately 12,522 thousand metric tons of limestone and 3,953 thousand metric tons of dolomite were consumed during production for these applications. Overall, usage of limestone and dolomite resulted in aggregate CO₂ emissions of 7.4 Tg CO₂ Eq. (7,397 Gg) (see Table 4-20 and Table 4-21). Emissions in 2005 increased 10 percent from the previous year and have increased 34 percent overall from 1990 through 2005.

Table 4-20: CO₂ Emissions from Limestone & Dolomite Use (Tg CO₂ Eq.)

Activity	1990	1995	2000	2001	2002	2003	2004	2005
Flux Stone	3.0	4.0	2.8	2.5	2.4	2.1	4.1	3.3
Glass Making	0.2	0.5	0.4	0.1	0.1	0.3	0.4	0.4
FGD	1.4	1.7	1.8	2.6	2.8	1.9	1.9	3.0
Magnesium Production	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.0
Other Miscellaneous Uses	0.8	1.1	0.9	0.5	0.7	0.4	0.4	0.7
Total	5.5	7.4	6.0	5.7	5.9	4.7	6.7	7.4

Notes: Totals may not sum due to independent rounding. "Other miscellaneous uses" include chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

Table 4-21: CO₂ Emissions from Limestone & Dolomite Use (Gg)

Activity	1990	1995	2000	2001	2002	2003	2004	2005
Flux Stone	2,999	4,004	2,830	2,514	2,405	2,072	4,112	3,265

⁶ Limestone and dolomite are collectively referred to as limestone by the industry, and intermediate varieties are seldom distinguished.

Limestone	2,554	3,077	1,810	1,640	1,330	904	2,023	1,398
Dolomite	446	927	1,020	874	1,075	1,168	2,088	1,867
Glass Making	217	533	368	113	61	337	350	427
Limestone	189	410	368	113	61	337	350	406
Dolomite	28	122	0	0	0	0	0	21
FGD	1,433	1,663	1,774	2,551	2,766	1,932	1,871	2,985
Magnesium Production	64	41	73	53	0	0	0	0
Other Miscellaneous Uses	819	1,119	916	501	652	380	369	721
Total	5,533	7,359	5,960	5,733	5,885	4,720	6,702	7,397

Notes: Totals may not sum due to independent rounding. Other miscellaneous uses include chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

Methodology

CO₂ emissions were calculated by multiplying the quantity of limestone or dolomite consumed by the average C content, approximately 12.0 percent for limestone and 13.2 percent for dolomite (based on stoichiometry). This assumes that all C is oxidized and released. This methodology was used for flux stone, glass manufacturing, flue gas desulfurization systems, chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining and then converting to CO₂ using a molecular weight ratio.

Traditionally, the production of magnesium metal was the only other use of limestone and dolomite that produced CO₂ emissions. At the start of 2001, there were two magnesium production plants operating in the United States and they used different production methods. One plant produced magnesium metal using a dolomitic process that resulted in the release of CO₂ emissions, while the other plant produced magnesium from magnesium chloride using a CO₂-emissions-free process called electrolytic reduction. However, the plant utilizing the dolomitic process ceased its operations prior to the end of 2001, so beginning in 2002 there were no emissions from this particular sub-use.

Consumption data for 1990 through 2005 of limestone and dolomite used for flux stone, glass manufacturing, flue gas desulfurization systems, chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining (see Table 4-22) were obtained from personal communication with Deborah Weaver of the USGS (Weaver 2006) and in the USGS *Minerals Yearbook: Crushed Stone Annual Report* (USGS 1993, 1995a, 1995b, 1996a, 1997a, 1998a, 1999a, 2000a, 2001a, 2002a, 2003a, 2004a, 2005a). The production capacity data for 1990 through 2005 of dolomitic magnesium metal (see Table 4-23) also came from the USGS (1995c, 1996b, 1997b, 1998b, 1999b, 2000b, 2001b, 2002b, 2003b, 2004b, 2005b, 2006). The last plant in the United States that used the dolomitic production process for magnesium metal closed in 2001. The USGS does not mention this process in the 2005 *Minerals Yearbook: Magnesium*; therefore, it is assumed that this process continues to be non-existent in the United States (USGS 2006). During 1990 and 1992, the USGS did not conduct a detailed survey of limestone and dolomite consumption by end-use. Consumption for 1990 was estimated by applying the 1991 percentages of total limestone and dolomite use constituted by the individual limestone and dolomite uses to 1990 total use. Similarly, the 1992 consumption figures were approximated by applying an average of the 1991 and 1993 percentages of total limestone and dolomite use constituted by the individual limestone and dolomite uses to the 1992 total.

Additionally, each year the USGS withholds data on certain limestone and dolomite end-uses due to confidentiality agreements regarding company proprietary data. For the purposes of this analysis, emissive end-uses that contained withheld data were estimated using one of the following techniques: (1) the value for all the withheld data points for limestone or dolomite use was distributed evenly to all withheld end-uses; (2) the average percent of total limestone or dolomite for the withheld end-use in the preceding and succeeding years; or (3) the average fraction of total limestone or dolomite for the end-use over the entire time period.

Finally, there is a large quantity of crushed stone reported to the USGS under the category “unspecified uses.” A portion of this consumption is believed to be limestone or dolomite used for emissive end uses. The quantity listed for “unspecified uses” was, therefore, allocated to each reported end-use according to each end uses fraction of total consumption in that year.⁷

Table 4-22: Limestone and Dolomite Consumption (Thousand Metric Tons)

Activity	1990	1995	2000	2001	2002	2003	2004	2005
Flux Stone	6,738	8,935	6,249	5,558	5,275	4,501	8,971	7,086
Limestone	5,804	6,995	4,114	3,727	3,023	2,055	4,599	3,176
Dolomite	933	1,941	2,135	1,831	2,252	2,466	4,373	3,910
Glass Making	489	1,189	836	258	139	765	796	966
Limestone	430	933	836	258	139	765	796	923
Dolomite	59	256	0	0	0	0	0	43
FGD	3,258	3,779	4,031	5,798	6,286	4,390	4,253	6,785
Other Miscellaneous Uses	1,835	2,543	2,081	1,138	1,483	863	840	1,638
Total	12,319	16,445	13,197	12,751	13,183	10,520	14,859	16,475

Notes: "Other miscellaneous uses" includes chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining. Zero values for limestone and dolomite consumption for glass making result during years when the USGS reports that no limestone or dolomite are consumed for this use.

Table 4-23: Dolomitic Magnesium Metal Production Capacity (Metric Tons)

Year	Production Capacity
1990	35,000
1995	22,222
2000	40,000
2001	29,167
2002	0
2003	0
2004	0
2005	0

Note: Production capacity for 2002, 2003, 2004, and 2005 amounts to zero because the last U.S. production plant employing the dolomitic process shut down mid-2001 (USGS 2002b, 2003b, 2004b, 2005b, 2006).

Uncertainty

The uncertainty levels presented in this section arise in part due to variations in the chemical composition of limestone. In addition to calcium carbonate, limestone may contain smaller amounts of magnesia, silica, and sulfur. The exact specifications for limestone or dolomite used as flux stone vary with the pyrometallurgical process, the kind of ore processed, and the final use of the slag. Similarly, the quality of the limestone used for glass manufacturing will depend on the type of glass being manufactured.

The estimates below also account for uncertainty associated with activity data. Much of the limestone consumed in the United States is reported as “other unspecified uses;” therefore, it is difficult to accurately allocate this unspecified quantity to the correct end-uses. Also, some of the limestone reported as “limestone” is believed to actually be dolomite, which has a higher C content. Additionally, there is significant inherent uncertainty associated with estimating withheld data points for specific end uses of limestone and dolomite. Lastly, the uncertainty of the estimates for limestone used in glass making is especially high. Large fluctuations in reported consumption exist,

⁷ This approach was recommended by USGS.

reflecting year-to-year changes in the number of survey responders. The uncertainty resulting from a shifting survey population is exacerbated by the gaps in the time series of reports. However, since glass making accounts for a small percent of consumption, its contribution to the overall emissions estimate is low.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-24. Limestone and Dolomite Use CO₂ emissions were estimated to be between 6.9 and 7.9 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 6 percent below and 6 percent above the emission estimate of 7.4 Tg CO₂ Eq.

Table 4-24: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Limestone and Dolomite Use (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission	Uncertainty Range Relative to Emission Estimate ^a			
		Estimate	(Tg CO ₂ Eq.)			
		(Tg CO ₂ Eq.)	(%)			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Limestone and Dolomite Use	CO ₂	7.4	6.9	7.9	-6%	+6%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Planned Improvements

Future improvements to the limestone and dolomite source category involve research into the availability of limestone and dolomite end-use data. If sufficient data are available, limestone and dolomite used as process materials in source categories to be included in future inventories (e.g., glass production, other process use of carbonates) may be removed and the emission estimates included there.

4.6. Soda Ash Manufacture and Consumption (IPCC Source Category 2A4)

Soda ash (sodium carbonate, Na₂CO₃) is a white crystalline solid that is readily soluble in water and strongly alkaline. Commercial soda ash is used as a raw material in a variety of industrial processes and in many familiar consumer products such as glass, soap and detergents, paper, textiles, and food. It is used primarily as an alkali, either in glass manufacturing or simply as a material that reacts with and neutralizes acids or acidic substances. Internationally, two types of soda ash are produced—natural and synthetic. The United States produces only natural soda ash and is second only to China in total soda ash-production. Trona is the principal ore from which natural soda ash is made.

Only three states produce natural soda ash: Wyoming, California, and Colorado. Of these three states, only net emissions of CO₂ from Wyoming were calculated due to specifics regarding the production processes employed in each state.⁸ During the production process used in Wyoming, trona ore is treated to produce soda ash. CO₂ is generated as a by-product of this reaction, and is eventually emitted into the atmosphere. In addition, CO₂ may also be released when soda ash is consumed.

⁸ In California, soda ash is manufactured using sodium carbonate-bearing brines instead of trona ore. To extract the sodium carbonate, the complex brines are first treated with CO₂ in carbonation towers to convert the sodium carbonate into sodium bicarbonate, which then precipitates from the brine solution. The precipitated sodium bicarbonate is then calcined back into sodium carbonate. Although CO₂ is generated as a by-product, the CO₂ is recovered and recycled for use in the carbonation stage and is not emitted.

In Colorado, the lone producer of sodium bicarbonate no longer mines trona in the state. Instead, NaHCO₃ is produced using soda ash feedstocks mined in Wyoming and shipped to Colorado. Because the trona is mined in Wyoming, the production numbers given by the USGS include the feedstocks mined in Wyoming and shipped to Colorado. In this way, the sodium bicarbonate production that takes place in Colorado is accounted for in the Wyoming numbers.

In 2005, CO₂ emissions from the manufacture of soda ash from trona were approximately 1.7 Tg CO₂ Eq. (1,655 Gg). Soda ash consumption in the United States generated 2.6 Tg CO₂ Eq. (2,573 Gg) in 2005. Total emissions from soda ash manufacture and consumption in 2005 were 4.2 Tg CO₂ Eq. (4,228 Gg) (see Table 4-25 and Table 4-26). Emissions have fluctuated since 1990. These fluctuations were strongly related to the behavior of the export market and the U.S. economy. Emissions in 2005 increased by approximately 0.5 percent from the previous year, and have increased overall by approximately 2 percent since 1990.

Table 4-25: CO₂ Emissions from Soda Ash Manufacture and Consumption (Tg CO₂ Eq.)

Year	Manufacture	Consumption	Total
1990	1.4	2.7	4.1
1995	1.6	2.7	4.3
2000	1.5	2.7	4.2
2001	1.5	2.6	4.1
2002	1.5	2.7	4.1
2003	1.5	2.6	4.1
2004	1.6	2.6	4.2
2005	1.7	2.6	4.2

Note: Totals may not sum due to independent rounding.

Table 4-26: CO₂ Emissions from Soda Ash Manufacture and Consumption (Gg)

Year	Manufacture	Consumption	Total
1990	1,431	2,710	4,141
1995	1,607	2,698	4,304
2000	1,529	2,652	4,181
2001	1,500	2,648	4,147
2002	1,470	2,668	4,139
2003	1,509	2,602	4,111
2004	1,607	2,598	4,205
2005	1,655	2,573	4,228

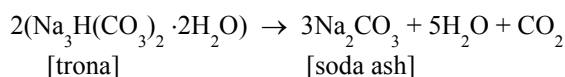
Note: Totals may not sum due to independent rounding.

The United States represents about one-fourth of total world soda ash output. The approximate distribution of soda ash by end-use in 2005 was glass making, 49 percent; chemical production, 27 percent; soap and detergent manufacturing, 10 percent; distributors, 5 percent; flue gas desulfurization, 2 percent; water treatment, 1 percent; pulp and paper production, 1 percent; and miscellaneous, 4 percent (USGS 2006).

Although the United States continues to be a major supplier of world soda ash, China, which surpassed the United States in soda ash production in 2003, is the world's leading producer. While Chinese soda ash production appears to be stabilizing, U.S. competition in Asian markets is expected to continue. Despite this competition, U.S. soda ash production is expected to increase by about 0.5 percent annually over the next five years. (USGS 2006).

Methodology

During the production process, trona ore is calcined in a rotary kiln and chemically transformed into a crude soda ash that requires further processing. CO₂ and water are generated as by-products of the calcination process. CO₂ emissions from the calcination of trona can be estimated based on the following chemical reaction:



Based on this formula, approximately 10.27 metric tons of trona are required to generate one metric ton of CO₂. Thus, the 17 million metric tons of trona mined in 2005 for soda ash production (USGS 2006) resulted in CO₂ emissions of approximately 1.7 Tg CO₂ Eq. (1,655 Gg).

Once manufactured, most soda ash is consumed in glass and chemical production, with minor amounts in soap and detergents, pulp and paper, flue gas desulfurization and water treatment. As soda ash is consumed for these purposes, additional CO₂ is usually emitted. In these applications, it is assumed that one mole of C is released for every mole of soda ash used. Thus, approximately 0.113 metric tons of C (or 0.415 metric tons of CO₂) are released for every metric ton of soda ash consumed.

The activity data for trona production and soda ash consumption (see Table 4-27) were taken from USGS (1994 through 2006). Soda ash manufacture and consumption data were collected by the USGS from voluntary surveys of the U.S. soda ash industry.

Table 4-27: Soda Ash Manufacture and Consumption (Gg)

Year	Manufacture*	Consumption
1990	14,700	6,530
1995	16,500	6,500
2000	15,700	6,390
2001	15,400	6,380
2002	15,100	6,430
2003	15,500	6,270
2004	16,500	6,260
2005	17,000	6,200

* Soda ash manufactured from trona ore only.

Uncertainty

Emission estimates from soda ash manufacture have relatively low associated uncertainty levels in that reliable and accurate data sources are available for the emission factor and activity data. The primary source of uncertainty, however, results from the fact that emissions from soda ash consumption are dependent upon the type of processing employed by each end-use. Specific information characterizing the emissions from each end-use is limited. Therefore, there is uncertainty surrounding the emission factors from the consumption of soda ash.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-28. Soda Ash Manufacture and Consumption CO₂ emissions were estimated to be between 3.9 and 4.5 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 7 percent below and 7 percent above the emission estimate of 4.2 Tg CO₂ Eq.

Table 4-28: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Soda Ash Manufacture and Consumption (Tg CO₂ Eq. and Percent)

Source	Gas	2005	Uncertainty Range Relative to Emission Estimate ^a			
		Emission	Range		Relative to Emission Estimate ^a	
		Estimate (Tg CO ₂ Eq.)	(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Soda Ash Manufacture and Consumption	CO ₂	4.2	3.9	4.5	-7%	+7%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

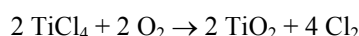
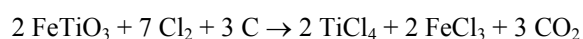
Planned Improvements

Future inventories are anticipated to estimate emissions from glass production and other use of carbonates. These inventories will extract soda ash consumed for glass production and other use of carbonates from the current soda ash consumption emission estimates and include them under those sources.

4.7. Titanium Dioxide Production (IPCC Source Category 2B5)

Titanium dioxide (TiO₂) is a metal oxide manufactured from titanium ore, and is principally used as a pigment. Titanium dioxide is a principal ingredient in white paint, and is also used as a pigment in the manufacture of white paper, foods, and other products. There are two processes for making TiO₂: the chloride process and the sulfate process. The chloride process uses petroleum coke and chlorine as raw materials and emits process-related CO₂. The sulfate process does not use petroleum coke or other forms of C as a raw material and does not emit CO₂.

The chloride process is based on the following chemical reactions:



The C in the first chemical reaction is provided by petroleum coke, which is oxidized in the presence of the chlorine and FeTiO₃ (the Ti-containing ore) to form CO₂. The majority of U.S. TiO₂ was produced in the United States through the chloride process, and a special grade of petroleum coke is manufactured specifically for this purpose.

Emissions of CO₂ in 2005 were 1.9 Tg CO₂ Eq. (1,921 Gg), a decrease of 18 percent from the previous year and an increase of 47 percent since 1990. The trend upward, due to increasing production within the industry, was disrupted in 2005 as a result of Hurricane Katrina (see Table 4-29), which disrupted production of titanium dioxide pigment in Mississippi (USGS 2006).

Table 4-29: CO₂ Emissions from Titanium Dioxide (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	1.3	1,308
1995	1.7	1,670
2000	1.9	1,918
2001	1.9	1,857
2002	2.0	1,997
2003	2.0	2,013
2004	2.3	2,259
2005	1.9	1,921

Methodology

Emissions of CO₂ from TiO₂ production were calculated by multiplying annual TiO₂ production by chloride-process-specific emission factors.

Data were obtained for the total amount of TiO₂ produced each year. For years previous to 2004, it was assumed that TiO₂ was produced using the chloride process and the sulfate process in the same ratio as the ratio of the total U.S. production capacity for each process. As of 2004, the last remaining sulfate-process plant in the United States closed. As a result, all U.S. current TiO₂ production results from the chloride process (USGS 2005). An emission factor of 0.4 metric tons C/metric ton TiO₂ was applied to the estimated chloride-process production. It was assumed that all TiO₂ produced using the chloride process was produced using petroleum coke, although some TiO₂ may have been produced with graphite or other C inputs. The amount of petroleum coke consumed annually in

TiO₂ production was calculated based on the assumption that petroleum coke used in the process is 90 percent C and 10 percent inert materials.

The emission factor for the TiO₂ chloride process was taken from the report, *Everything You've Always Wanted to Know about Petroleum Coke* (Onder and Bagdoyan 1993). Titanium dioxide production data and the percentage of total TiO₂ production capacity that is chloride process for 1990 through 2005 (see Table 4-30) were obtained from a personal communication with Deborah Kramer, USGS Commodity Specialist, of the USGS (Kramer 2006) and through the *Minerals Yearbook: Titanium Annual Report* (USGS 1991 through 2005). Percentage chloride-process data were not available for 1990 through 1993, and data from the 1994 USGS *Minerals Yearbook* were used for these years. Because a sulfate-process plant closed in September 2001, the chloride-process percentage for 2001 was estimated based on a discussion with Joseph Gambogi (2002). By 2002, only one sulfate plant remained online in the United States and this plant closed in 2004 (USGS 2005). The composition data for petroleum coke were obtained from Onder and Bagdoyan (1993).

Table 4-30: Titanium Dioxide Production (Gg)

Year	Gg
1990	979
1995	1,250
2000	1,400
2001	1,330
2002	1,410
2003	1,420
2004	1,540
2005	1,310

Uncertainty

Although some TiO₂ may be produced using graphite or other C inputs, information and data regarding these practices were not available. Titanium dioxide produced using graphite inputs, for example, may generate differing amounts of CO₂ per unit of TiO₂ produced as compared to that generated through the use of petroleum coke in production. While the most accurate method to estimate emissions would be to base calculations on the amount of reducing agent used in each process rather than on the amount of TiO₂ produced, sufficient data were not available to do so.

Also, annual TiO₂ is not reported by USGS by the type of production process used (chloride or sulfate). Only the percentage of total production capacity by process is reported. The percent of total TiO₂ production capacity that was attributed to the chloride process was multiplied by total TiO₂ production to estimate the amount of TiO₂ produced using the chloride process (since, as of 2004, the last remaining sulfate-process plant in the United States closed). This assumes that the chloride-process plants and sulfate-process plants operate at the same level of utilization. Finally, the emission factor was applied uniformly to all chloride-process production, and no data were available to account for differences in production efficiency among chloride-process plants. In calculating the amount of petroleum coke consumed in chloride-process TiO₂ production, literature data were used for petroleum coke composition. Certain grades of petroleum coke are manufactured specifically for use in the TiO₂ chloride process; however, this composition information was not available.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-31. Titanium dioxide consumption CO₂ emissions were estimated to be between 1.6 and 2.2 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 16 percent below and 16 percent above the emission estimate of 1.9 Tg CO₂ Eq.

Table 4-31: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Titanium Dioxide Production (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Titanium Dioxide Production	CO ₂	1.9	1.6	2.2	-16%	+16%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

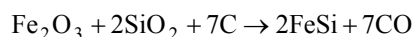
Planned Improvements

Future improvements to TiO₂ production methodology include researching the significance of titanium-slag production in electric furnaces and synthetic-rutile production using the Becher process in the United States. Significant use of these production processes will be included in future estimates.

4.8. Ferroalloy Production (IPCC Source Category 2C2)

CO₂ and CH₄ are emitted from the production of several ferroalloys. Ferroalloys are composites of iron and other elements such as silicon, manganese, and chromium. When incorporated in alloy steels, ferroalloys are used to alter the material properties of the steel. Estimates from two types of ferrosilicon (25 to 55 percent and 56 to 95 percent silicon), silicon metal (about 98 percent silicon), and miscellaneous alloys (36 to 65 percent silicon) have been calculated. Emissions from the production of ferrochromium and ferromanganese are not included here because of the small number of manufacturers of these materials in the United States. Subsequently, government information disclosure rules prevent the publication of production data for these production facilities.

Similar to emissions from the production of iron and steel, CO₂ is emitted when metallurgical coke is oxidized during a high-temperature reaction with iron and the selected alloying element. Due to the strong reducing environment, CO is initially produced, and eventually oxidized to CO₂. A representative reaction equation for the production of 50 percent ferrosilicon is given below:



While most of the C contained in the process materials is released to the atmosphere as CO₂, a percentage is also released as CH₄ and other volatiles. The amount of CH₄ that is released is dependent on furnace efficiency, operation technique, and control technology.

Emissions of CO₂ from ferroalloy production in 2005 were 1.4 Tg CO₂ Eq. (1,392 Gg) (see Table 4-32 and Table 4-33), which is a 2 percent decrease from the previous year and a 35 percent reduction since 1990. Emissions of CH₄ from ferroalloy production in 2005 were 0.01 Tg CO₂ Eq. (0.4 Gg), which is a 1 percent decrease from the previous year and a 43 percent decrease since 1990.

Table 4-32: CO₂ and CH₄ Emissions from Ferroalloy Production (Tg CO₂ Eq.)

Year	1990	1995	2000	2001	2002	2003	2004	2005
CO ₂	2.2	2.0	1.9	1.5	1.3	1.3	1.4	1.4
CH ₄	+	+	+	+	+	+	+	+
Total	2.2	2.0	1.9	1.5	1.4	1.3	1.4	1.4

+ Does not exceed 0.05 Tg CO₂ Eq.

Note: Totals may not sum due to independent rounding.

Table 4-33: CO₂ and CH₄ Emissions from Ferroalloy Production (Gg)

Year	1990	1995	2000	2001	2002	2003	2004	2005
CO ₂	2,152	2,036	1,893	1,459	1,349	1,305	1,419	1,392
CH ₄	0.7	0.6	0.5	0.4	0.4	0.4	0.4	0.4

Methodology

Emissions of CO₂ and CH₄ from ferroalloy production were calculated by multiplying annual ferroalloy production by material-specific emission factors. Emission factors taken from the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006) were applied to ferroalloy production. For ferrosilicon alloys containing 25 to 55 percent silicon and miscellaneous alloys (including primarily magnesium-ferrosilicon, but also including other silicon alloys) containing 32 to 65 percent silicon, an emission factor for 45 percent silicon was applied for CO₂ (2.5 metric tons CO₂/metric ton of alloy produced) and an emission factor for 65 percent silicon was applied for CH₄ (1 kg CO₂/metric ton of alloy produced). Additionally, for ferrosilicon alloys containing 56 to 95 percent silicon, an emission factor for 75 percent silicon ferrosilicon was applied for both CO₂ and CH₄ (4 metric tons CO₂/metric ton alloy produced and 1 kg CH₄/metric ton of alloy produced, respectively). The emission factors for silicon metal equaled 5 tons CO₂/metric ton metal produced and 1.2 kg CH₄/metric ton metal produced. It was assumed that 100 percent of the ferroalloy production was produced using petroleum coke using an electric arc furnace process (IPCC 2006), although some ferroalloys may have been produced with coking coal, wood, other biomass, or graphite C inputs. The amount of petroleum coke consumed in ferroalloy production was calculated assuming that the petroleum coke used is 90 percent C and 10 percent inert material.

Ferroalloy production data for 1990 through 2005 (see Table 4-34) were obtained from the USGS through personal communications with the USGS Silicon Commodity Specialist (Corathers 2006) and through the *Minerals Yearbook: Silicon Annual Report* (USGS 1991 through 2005). Until 1999, the USGS reported production of ferrosilicon containing 25 to 55 percent silicon separately from production of miscellaneous alloys containing 32 to 65 percent silicon; beginning in 1999, the USGS reported these as a single category (see Table 4-34). The composition data for petroleum coke was obtained from Onder and Bagdoyan (1993).

Table 4-34: Production of Ferroalloys (Metric Tons)

Year	Ferrosilicon 25%-55%	Ferrosilicon 56%-95%	Silicon Metal	Misc. Alloys 32-65%
1990	321,385	109,566	145,744	72,442
1995	184,000	128,000	163,000	99,500
2000	229,000	100,000	184,000	NA
2001	167,000	89,000	137,000	NA
2002	156,000	98,600	113,000	NA
2003	115,000	80,500	139,000	NA
2004	120,000	92,300	150,000	NA
2005	123,000	86,100	148,000	NA

NA (Not Available)

Uncertainty

Although some ferroalloys may be produced using wood or other biomass as a C source, information and data regarding these practices were not available. Emissions from ferroalloys produced with wood or other biomass would not be counted under this source because wood-based C is of biogenic origin.⁹ Even though emissions from ferroalloys produced with coking coal or graphite inputs would be counted in national trends, they may be generated with varying amounts of CO₂ per unit of ferroalloy produced. The most accurate method for these estimates would be to base calculations on the amount of reducing agent used in the process, rather than the amount of ferroalloys produced. These data, however, were not available.

⁹ Emissions and sinks of biogenic carbon are accounted for in the Land-Use Change, and Forestry chapter.

Emissions of CH₄ from ferroalloy production will vary depending on furnace specifics, such as type, operation technique, and control technology. Higher heating temperatures and techniques such as sprinkle charging will reduce CH₄ emissions; however, specific furnace information was not available or included in the CH₄ emission estimates.

Also, annual ferroalloy production is now reported by the USGS in three broad categories: ferroalloys containing 25 to 55 percent silicon (including miscellaneous alloys), ferroalloys containing 56 to 95 percent silicon, and silicon metal. It was assumed that the IPCC emission factors apply to all of the ferroalloy production processes, including miscellaneous alloys. Finally, production data for silvery pig iron (alloys containing less than 25 percent silicon) are not reported by the USGS to avoid disclosing company proprietary data. Emissions from this production category, therefore, were not estimated.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-35. Ferroalloy production CO₂ emissions were estimated to be between 1.2 and 1.6 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 13 percent below and 13 percent above the emission estimate of 1.4 Tg CO₂ Eq. Ferroalloy production CH₄ emissions were estimated to be between a range of approximately 12 percent below and 12 percent above the emission estimate of 0.01 Tg CO₂ Eq. .

Table 4-35: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Ferroalloy Production (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ferroalloy Production	CO ₂	1.4	1.2	1.6	-13%	+13%
Ferroalloy Production	CH ₄	+	+	+	-12%	+12%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

+ Does not exceed 0.05 Tg CO₂ Eq.

Recalculations Discussion

Estimates of CO₂ emissions from ferroalloy production were revised for the entire time series to reflect updated emission factors based on the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006). This change resulted in a 9.5 percent (0.2 Tg CO₂ Eq.) increase in emissions on average throughout the timeseries. Estimates of CH₄ emissions are included for the first time during the current inventory year.

Planned Improvements

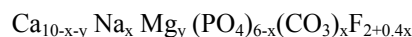
Future improvements to the ferroalloy production source category include research into the data availability for ferroalloys other than ferrosilicon and silicon metal. If data are available, emissions will be estimated for those ferroalloys. Additionally, research will be conducted to determine whether data are available concerning raw material consumption (e.g., coal coke, limestone and dolomite flux, etc.) for inclusion in ferroalloy production emission estimates.

4.9. Phosphoric Acid Production (IPCC Source Category 2B5)

Phosphoric acid (H₃PO₄) is a basic raw material in the production of phosphate-based fertilizers. Phosphate rock is mined in Florida, North Carolina, Idaho, Utah, and other areas of the United States and is used primarily as a raw material for phosphoric acid production. The production of phosphoric acid from phosphate rock produces byproduct gypsum (CaSO₄-2H₂O), referred to as phosphogypsum.

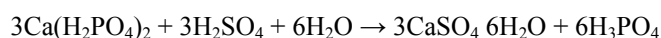
The composition of natural phosphate rock varies depending upon the location where it is mined. Natural phosphate rock mined in the United States generally contains inorganic C in the form of calcium carbonate

(limestone) and also may contain organic C. The chemical composition of phosphate rock (francolite) mined in Florida is:

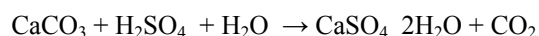


The calcium carbonate component of the phosphate rock is integral to the phosphate rock chemistry. Phosphate rock can also contain organic C that is physically incorporated into the mined rock but is not an integral component of the phosphate rock chemistry. Phosphoric acid production from natural phosphate rock is a source of CO₂ emissions, due to the chemical reaction of the inorganic C (calcium carbonate) component of the phosphate rock.

The phosphoric acid production process involves chemical reaction of the calcium phosphate (Ca₃(PO₄)₂) component of the phosphate rock with sulfuric acid (H₂SO₄) and recirculated phosphoric acid (H₃PO₄) (EFMA 1997). The primary chemical reactions for the production of phosphoric acid from phosphate rock are:



The limestone (CaCO₃) component of the phosphate rock reacts with the sulfuric acid in the phosphoric acid production process to produce calcium sulfate (phosphogypsum) and CO₂. The chemical reaction for the limestone-sulfuric acid reaction is:



Total marketable phosphate rock production in 2005 was 36.0 million metric tons. Approximately 87 percent of domestic phosphate rock production was mined in Florida and North Carolina, while approximately 13 percent of production was mined in Idaho and Utah. In addition, 2.6 million metric tons of crude phosphate rock was imported for consumption in 2005. Marketable phosphate rock production, including domestic production and imports for consumption, decreased by approximately 1.0 percent between 2004 and 2005. However, over the 1990 to 2005 period, production decreased by 12 percent. The 35.3 million metric tons produced in 2001 was the lowest production level recorded since 1965 and was driven by a worldwide decrease in demand for phosphate fertilizers. Total CO₂ emissions from phosphoric acid production were 1.4 Tg CO₂ Eq. (1,383 Gg) in 2005 (see Table 4-36).

Table 4-36: CO₂ Emissions from Phosphoric Acid Production (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	1.5	1,529
1995	1.5	1,513
2000	1.4	1,382
2001	1.3	1,264
2002	1.3	1,338
2003	1.4	1,382
2004	1.4	1,395
2005	1.4	1,383

Methodology

CO₂ emissions from production of phosphoric acid from phosphate rock is calculated by multiplying the average amount of calcium carbonate contained in the natural phosphate rock by the amount of phosphate rock that is used annually to produce phosphoric acid, accounting for domestic production and net imports for consumption.

From 1993 to 2004, the *USGS Mineral Yearbook: Phosphate Rock* disaggregated phosphate rock mined annually in Florida and North Carolina phosphate rock mined annually in Idaho and Utah, and reported the annual amounts of

phosphate rock exported and imported for consumption (see Table 4-37). For the years 1990, 1991, 1992, and 2005, only nationally aggregated mining data was reported by USGS. For these years, the breakdown of phosphate rock mined in Florida and North Carolina, and the amount mined in Idaho and Utah, are approximated using 1993 to 2004 data. Data for domestic production of phosphate rock, exports of phosphate rock, and imports of phosphate rock for consumption for 1990 through 2005 were obtained from *USGS Minerals Yearbook: Phosphate Rock* (USGS 1994 through 2006). In 2004 and 2005, the USGS reported no exports of phosphate rock from U.S. producers (USGS 2005, 2006).

The carbonate content of phosphate rock varies depending upon where the material is mined. Composition data for domestically mined and imported phosphate rock were provided by the Florida Institute of Phosphate Research (FIPR 2003). Phosphate rock mined in Florida contains approximately 1 percent inorganic C, and phosphate rock imported from Morocco contains approximately 1.46 percent inorganic C. Calcined phosphate rock mined in North Carolina and Idaho contains approximately 0.41 percent and 0.27 percent inorganic C, respectively (see Table 4-38).

Carbonate content data for phosphate rock mined in Florida are used to calculate the CO₂ emissions from consumption of phosphate rock mined in Florida and North Carolina (87 percent of domestic production) and carbonate content data for phosphate rock mined in Morocco are used to calculate CO₂ emissions from consumption of imported phosphate rock. The CO₂ emissions calculation is based on the assumption that all of the domestic production of phosphate rock is used in uncalcined form. At last reporting, the USGS noted that one phosphate rock producer in Idaho produces calcined phosphate rock; however, no production data were available for this single producer (USGS 2005). Carbonate content data for uncalcined phosphate rock mined in Idaho and Utah (13 percent of domestic production) were not available, and carbonate content was therefore estimated from the carbonate content data for calcined phosphate rock mined in Idaho.

The CO₂ emissions calculation methodology is based on the assumption that all of the inorganic C (calcium carbonate) content of the phosphate rock reacts to CO₂ in the phosphoric acid production process and is emitted with the stack gas. The methodology also assumes that none of the organic C content of the phosphate rock is converted to CO₂ and that all of the organic C content remains in the phosphoric acid product.

Table 4-37: Phosphate Rock Domestic Production, Exports, and Imports (Gg)

Location/Year	1990	1995	2000	2001	2002	2003	2004	2005
U.S. Production ^a	49,800	43,720	37,370	32,830	34,720	36,410	36,530	36,000
FL & NC	42,494	38,100	31,900	28,100	29,800	31,300	31,600	31,140
ID & UT	7,306	5,620	5,470	4,730	4,920	5,110	4,930	4,860
Exports—FL & NC	6,240	2,760	299	9	62	64	-	-
Imports—Morocco	451	1,800	1,930	2,500	2,700	2,400	2,500	2,630
Total U.S. Consumption	44,011	42,760	39,001	35,321	37,358	38,746	39,030	38,630

^a USGS does not disaggregate production data regionally (FL & NC and ID & UT) for 1990 and 2005. Data for those years are estimated based on the remaining time series distribution.

- Assumed equal to zero.

Table 4-38: Chemical Composition of Phosphate Rock (percent by weight)

Composition	Central Florida	North Florida	North Carolina (calcined)	Idaho (calcined)	Morocco
Total Carbon (as C)	1.60	1.76	0.76	0.60	1.56
Inorganic Carbon (as C)	1.00	0.93	0.41	0.27	1.46
Organic Carbon (as C)	0.60	0.83	0.35	-	0.10
Inorganic Carbon (as CO ₂)	3.67	3.43	1.50	1.00	5.00

Source: FIPR 2003

- Assumed equal to zero.

Uncertainty

Phosphate rock production data used in the emission calculations are developed by the USGS through monthly and semiannual voluntary surveys of the active phosphate rock mines during 2005. For previous years in the timeseries, USGS provided the data disaggregated regionally; however, for 2005 only total U.S. phosphate rock production were reported. Regional production for 2005 was estimated based on regional-production data from previous the year and multiplied by regionally-specific emission factors. There is uncertainty associated with the degree to which the estimated 2005 regional-production data represents actual production in those regions. Total U.S. phosphate rock production data are not considered to be a significant source of uncertainty because all the domestic phosphate rock producers report their annual production to the USGS. Data for imports for consumption and exports of phosphate rock used in the emission calculation are based on international trade data collected by the U.S. Census Bureau. These U.S. government economic data are not considered to be a significant source of uncertainty.

An additional source of uncertainty in the calculation of CO₂ emissions from phosphoric acid production is the carbonate composition of phosphate rock; the composition of phosphate rock varies depending upon where the material is mined, and may also vary over time. Another source of uncertainty is the disposition of the organic C content of the phosphate rock. A representative of the FIPR indicated that in the phosphoric acid production process, the organic C content of the mined phosphate rock generally remains in the phosphoric acid product, which is what produces the color of the phosphoric acid product (FIPR 2003a). Organic C is therefore not included in the calculation of CO₂ emissions from phosphoric acid production.

A third source of uncertainty is the assumption that all domestically-produced phosphate rock is used in phosphoric acid production and used without first being calcined. Calcination of the phosphate rock would result in conversion of some of the organic C in the phosphate rock into CO₂. However, according to the USGS, only one producer in Idaho is currently calcining phosphate rock, and no data were available concerning the annual production of this single producer (USGS 2005). For available years, total production of phosphate rock in Utah and Idaho combined amounts to approximately 13 percent of total domestic production on average (USGS 1994 through 2005).

Finally, USGS indicated that 10 percent of domestically-produced phosphate rock is used to manufacture elemental phosphorus and other phosphorus-based chemicals, rather than phosphoric acid (USGS 2006). According to USGS, there is only one domestic producer of elemental phosphorus, in Idaho, and no data were available concerning the annual production of this single producer. Elemental phosphorus is produced by reducing phosphate rock with coal coke, and it is therefore assumed that 100 percent of the carbonate content of the phosphate rock will be converted to CO₂ in the elemental phosphorus production process. The calculation for CO₂ emissions is based on the assumption that phosphate rock consumption, for purposes other than phosphoric acid production, results in CO₂ emissions from 100 percent of the inorganic C content in phosphate rock, but none from the organic C content. This phosphate rock, consumed for other purposes, constitutes approximately 10 percent of total phosphate rock consumption.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-39. Phosphoric acid production CO₂ emissions were estimated to be between 1.1 and 1.6 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 18 percent below and 19 percent above the emission estimate of 1.4 Tg CO₂ Eq.

Table 4-39: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Phosphoric Acid Production (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Phosphoric Acid Production	CO ₂	1.4	1.1	1.6	-18%	+19%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

4.10. Carbon Dioxide Consumption (IPCC Source Category 2B5)

CO₂ is used for a variety of commercial applications, including food processing, chemical production, carbonated beverage production, and refrigeration, and is also used in petroleum production for enhanced oil recovery (EOR). CO₂ used for EOR is injected into the underground reservoirs to increase the reservoir pressure to enable additional petroleum to be produced.

For the most part, CO₂ used in non-EOR applications will eventually be released to the atmosphere, and for the purposes of this analysis CO₂ used in commercial applications other than EOR is assumed to be emitted to the atmosphere. CO₂ used in EOR applications is discussed in the Energy Chapter under “Carbon Capture and Storage, including Enhanced Oil Recovery” and is not discussed in this section.

CO₂ is produced from naturally occurring CO₂ reservoirs, as a by-product from the energy and industrial production processes (e.g., ammonia production, fossil fuel combustion, ethanol production), and as a by-product from the production of crude oil and natural gas, which contain naturally occurring CO₂ as a component. Only CO₂ produced from naturally occurring CO₂ reservoirs and used in industrial applications other than EOR is included in this analysis. Neither by-product CO₂ generated from energy or industrial production processes nor CO₂ separated from crude oil and natural gas are included in this analysis for a number of reasons. CO₂ captured from biogenic sources (e.g., ethanol production plants) is not included in the inventory. CO₂ captured from crude oil and gas production is used in EOR applications and is therefore reported in the Energy Chapter. Any CO₂ captured from industrial or energy production processes (e.g., ammonia plants, fossil fuel combustion) and used in non-EOR applications is assumed to be emitted to the atmosphere. The CO₂ emissions from such capture and use are therefore accounted for under Ammonia Production, Fossil Fuel Combustion, or other appropriate source category.

CO₂ is produced as a by-product of crude oil and natural gas production. This CO₂ is separated from the crude oil and natural gas using gas processing equipment, and may be emitted directly to the atmosphere, or captured and reinjected into underground formations, used for EOR, or sold for other commercial uses. A further discussion of CO₂ used in EOR is described in the Energy Chapter under “Box 3-3 Carbon Dioxide Transport, Injection, and Geological Storage.” The only CO₂ consumption that is accounted for in this analysis is CO₂ produced from naturally-occurring CO₂ reservoirs that is used in commercial applications other than EOR.

There are currently two facilities, one in Mississippi and one in New Mexico, producing CO₂ from naturally occurring CO₂ reservoirs for use in both EOR and in other commercial applications (e.g., chemical manufacturing, food production). There are other naturally occurring CO₂ reservoirs, mostly located in the western U.S. Facilities are producing CO₂ from these natural reservoirs, but they are only producing CO₂ for EOR applications, not for other commercial applications (Allis et al. 2000). CO₂ production from these facilities is discussed in the Energy Chapter.

In 2005, the amount of CO₂ produced by the Mississippi and New Mexico facilities for commercial applications and subsequently emitted to the atmosphere were 1.3 Tg CO₂ Eq. (1,324 Gg) (see Table 4-40). This amount represents a increase of 10 percent from the previous year and a decrease of 6 percent from emissions in 1990. This decrease was due to a decrease in the percent of the Mississippi facility’s total reported production that was used for commercial applications. During this period the Mississippi facility dedicated more of its total production to EOR.

Table 4-40: CO₂ Emissions from CO₂ Consumption (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	1.4	1,415
1995	1.4	1,423
2000	1.4	1,416
2001	0.8	825
2002	1.0	978
2003	1.3	1,310
2004	1.2	1,199

2005 1.3 1,324

Methodology

CO₂ emission estimates for 1990 through 2005 were based on production data for the two facilities currently producing CO₂ from naturally-occurring CO₂ reservoirs for use in non-EOR applications. Some of the CO₂ produced by these facilities is used for EOR and some is used in other commercial applications (e.g., chemical manufacturing, food production). It is assumed that 100 percent of the CO₂ production used in commercial applications other than EOR is eventually released into the atmosphere.

CO₂ production data for the Jackson Dome, Mississippi facility and the percentage of total production that was used for EOR and in non-EOR applications were obtained from the Advanced Resources Institute (ARI 2006) for 1990 to 2000 and from the Annual Reports for Denbury Resources (Denbury Resources 2002, 2003, 2004, 2005, 2006) for 2001 to 2005. Denbury Resources reported the average CO₂ production in units of MMCF CO₂ per day for 2001 through 2005 and reported the percentage of the total average annual production that was used for EOR. CO₂ production data for the Bravo Dome, New Mexico facility were obtained from the New Mexico Bureau of Geology and Mineral Resources for the years 1990 through 2003 (Broadhead 2006). The New Mexico Bureau of Geology reported production in billion cubic feet per year. According to the New Mexico Bureau, the amount of CO₂ produced from Bravo Dome for use in non-EOR applications is less than one percent of total production (Broadhead 2003a). Production data for 2004 and 2005 were not available for Bravo Dome, so it is assumed that the production values for those years are equal to the 2003 value.

Table 4-41: CO₂ Production (Gg CO₂) and the Percent Used for Non-EOR Applications for Jackson Dome and Bravo Dome

Year	Jackson Dome CO ₂ Production (Gg)	Jackson Dome % Used for Non-EOR	Bravo Dome CO ₂ Production (Gg)	Bravo Dome % Used for Non-EOR
1990	1,353	100%	6,241	1%
1995	1,353	100%	7,003	1%
2000	1,353	100%	6,328	1%
2001	1,624	47%	6,196	1%
2002	2,010	46%	5,295	1%
2003	3,286	38%	6,090	1%
2004	4,214	27%	6,090	1%
2005	4,678	27%	6,090	1%

Uncertainty

Uncertainty is associated with the number of facilities that are currently producing CO₂ from naturally occurring CO₂ reservoirs for commercial uses other than EOR, and for which the CO₂ emissions are not accounted for elsewhere. Research indicates that there are only two such facilities, which are in New Mexico and Mississippi; however, additional facilities may exist that have not been identified. In addition, it is possible that CO₂ recovery exists in particular production and end-use sectors that are not accounted for elsewhere. Such recovery may or may not affect the overall estimate of CO₂ emissions from that sector depending upon the end use to which the recovered CO₂ is applied. Further research is required to determine whether CO₂ is being recovered from other facilities for application to end uses that are not accounted for elsewhere.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-42. CO₂ consumption CO₂ emissions were estimated to be between 1.1 and 1.6 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 16 percent below to 21 percent above the emission estimate of 1.3 Tg CO₂ Eq.

Table 4-42: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from CO₂ Consumption (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
CO ₂ Consumption	CO ₂	1.3	1.1	1.6	-16%	+21%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

Data for total Bravo Dome CO₂ production were updated for the entire time series based on new production data from the facility. Data for CO₂ production from Jackson Dome were provided for years 1990 through 2000 for the first time during the current inventory year. These changes resulted in an average emission increase of 70 percent for years 1990 through 2000 and an average emission increase of less than one percent for years 2001 to 2005.

4.11. Zinc Production (IPCC Source Category 2C5)

Zinc production in the United States consists of both primary and secondary processes. Primary production techniques used in the United States are the electro-thermic and electrolytic process while secondary techniques used in the United States include a range of metallurgical, hydrometallurgical, and pyrometallurgical processes. Worldwide primary zinc production also employs a pyrometallurgical process using the Imperial Smelting Furnace process; however, this process is not used in the United States (Sjardin 2003). Of the primary and secondary processes used in the United States, the electro-thermic process results in non-energy CO₂ emissions, as does the Waelz Kiln process—a technique used to produce secondary zinc from electric-arc furnace (EAF) dust (Viklund-White 2000).

During the electro-thermic zinc production process, roasted zinc concentrate and, when available, secondary zinc products enter a sinter feed where they are burned to remove impurities before entering an electric retort furnace. Metallurgical coke added to the electric retort furnace reduces the zinc oxides and produces vaporized zinc, which is then captured in a vacuum condenser. This reduction process produces non-energy CO₂ emissions (Sjardin 2003). The electrolytic zinc production process does not produce non-energy CO₂ emissions.

In the Waelz Kiln process, EAF dust, which is captured during the recycling of galvanized steel, enters a kiln along with a reducing agent—often metallurgical coke. When kiln temperatures reach approximately 1100-1200°C, zinc fumes are produced, which are combusted with air entering the kiln. This combustion forms zinc oxide, which is collected in a baghouse or electrostatic precipitator, and is then leached to remove chloride and fluoride. Through this process, approximately 0.33 tons of zinc are produced for every ton of EAF dust treated (Viklund-White 2000).

In 2005, U.S. primary and secondary zinc production totaled 540,200 metric tons (Gabby 2006). The resulting emissions of CO₂ from zinc production in 2005 were estimated to be 0.5 Tg CO₂ Eq. (460 Gg) (see Table 4-43). All 2005 CO₂ emissions result from secondary zinc production.

Table 4-43: CO₂ Emissions from Zinc Production (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	0.9	939
1995	1.0	1,003
2000	1.1	1,129
2001	1.0	976
2002	0.9	927
2003	0.5	502
2004	0.5	472
2005	0.5	460

After a gradual increase in total emissions from 1990 to 2000, largely due to an increase in secondary zinc production, 2005 emissions have decreased by nearly half that of 1990 (49 percent) due to the closing of an electro-thermic-process zinc plant in Monaca, PA (USGS 2004).

Methodology

Non-energy CO₂ emissions from zinc production result from those processes that use metallurgical coke or other C-based materials as reductants. Sjardin (2003) provides an emission factor of 0.43 metric tons CO₂/ton zinc produced for emissive zinc production processes; however, this emission factor is based on the Imperial Smelting Furnace production process. Because the Imperial Smelting Furnace production process is not used in the United States, emission factors specific to those emissive zinc production processes used in the United States, which consist of the electro-thermic and Waelz Kiln processes, were needed. Due to the limited amount of information available for these electro-thermic processes, only Waelz Kiln process-specific emission factors were developed. These emission factors were applied to both the Waelz Kiln process and the electro-thermic zinc production processes. A Waelz Kiln emission factor based on the amount of zinc produced was developed based on the amount of metallurgical coke consumed for non-energy purposes per ton of zinc produced, 1.19 metric tons coke/metric ton zinc produced (Viklund-White 2000), and the following equation:

$$EF_{\text{Waelz Kiln}} = \frac{1.19 \text{ metric tons coke}}{\text{metric tons zinc}} \times \frac{0.84 \text{ metric tons C}}{\text{metric ton coke}} \times \frac{3.67 \text{ metric tons CO}_2}{\text{metric ton C}} = \frac{3.66 \text{ metric tons CO}_2}{\text{metric ton zinc}}$$

The USGS disaggregates total U.S. primary zinc production capacity into zinc produced using the electro-thermic process and zinc produced using the electrolytic process; however, the USGS does not report the amount of zinc produced using each process, only the total zinc production capacity of the zinc plants using each process. The total electro-thermic zinc production capacity is divided by total primary zinc production capacity to estimate the percent of primary zinc produced using the electro-thermic process. This percent is then multiplied by total primary zinc production to estimate the amount of zinc produced using the electro-thermic process, and the resulting value is multiplied by the Waelz Kiln process emission factor to obtain total CO₂ emissions for primary zinc production. According to the USGS, the only remaining plant producing primary zinc using the electro-thermic process closed in 2003 (USGS 2004). Therefore, CO₂ emissions for primary zinc production are reported only for years 1990 through 2002.

In the United States, secondary zinc is produced through either the electro-thermic or Waelz Kiln process. In 1997, the Horsehead Corporation plant, located in Monaca, PA, produced 47,174 metric tons of secondary zinc using the electro-thermic process (Queneau et al. 1998). This is the only plant in the United States that uses the electro-thermic process to produce secondary zinc, which, in 1997, accounted for 13 percent of total secondary zinc production. This percentage was applied to all years within the time series up until the Monaca plant's closure in 2003 (USGS 2004) to estimate the total amount of secondary zinc produced using the electro-thermic process. This value is then multiplied by the Waelz Kiln process emission factor to obtain total CO₂ emissions for secondary zinc produced using the electro-thermic process.

U.S. secondary zinc is also produced by processing recycled EAF dust in a Waelz Kiln furnace. Due to the complexities of recovering zinc from recycled EAF dust, an emission factor based on the amount of EAF dust consumed rather than the amount of secondary zinc produced is believed to represent actual CO₂ emissions from the process more accurately (Stuart 2005). An emission factor based on the amount of EAF dust consumed was developed based on the amount of metallurgical coke consumed per ton of EAF dust consumed, 0.4 metric tons coke/metric ton EAF dust consumed (Viklund-White 2000), and the following equation:

$$EF_{\text{EAF Dust}} = \frac{0.4 \text{ metric tons coke}}{\text{metric tons EAF dust}} \times \frac{0.84 \text{ metric tons C}}{\text{metric ton coke}} \times \frac{3.67 \text{ metric tons CO}_2}{\text{metric ton C}} = \frac{1.23 \text{ metric tons CO}_2}{\text{metric ton EAF Dust}}$$

The Horsehead Corporation plant, located in Palmerton, PA, is the only large plant in the United States that produces secondary zinc by recycling EAF dust (Stuart 2005). In 2003, this plant consumed 408,240 metric tons of

EAF dust, producing 137,169 metric tons of secondary zinc (Recycling Today 2005). This zinc production accounted for 36 percent of total secondary zinc produced in 2003. This percentage was applied to the USGS data for total secondary zinc production for all years within the time series to estimate the total amount of secondary zinc produced by consuming recycled EAF dust in a Waelz Kiln furnace. This value is multiplied by the Waelz Kiln process emission factor for EAF dust to obtain total CO₂ emissions.

The 1990 through 2004 activity data for primary and secondary zinc production (see Table 4-44) were obtained through the USGS *Mineral Yearbook: Zinc* (USGS 1994 through 2005). Activity data for 2005 were obtained from the USGS Commodity Specialist (Gabby 2006).

Table 4-44: Zinc Production (Metric Tons)

Year	Primary	Secondary
1990	262,704	341,400
1995	231,840	353,000
2000	227,800	440,000
2001	203,000	375,000
2002	181,800	366,000
2003	186,900	381,000
2004	188,200	358,000
2005	191,200	349,000

Uncertainty

The uncertainties contained in these estimates are two-fold, relating to activity data and emission factors used.

First, there are uncertainties associated with the percent of total zinc production, both primary and secondary, that is attributed to the electro-thermic and Waelz Kiln emissive zinc production processes. For primary zinc production, the amount of zinc produced annually using the electro-thermic process is estimated from the percent of primary-zinc production capacity that electro-thermic production capacity constitutes for each year of the time series. This assumes that each zinc plant is operating at the same percentage of total production capacity, which may not be the case and this calculation could either overestimate or underestimate the percentage of the total primary zinc production that is produced using the electro-thermic process. The amount of secondary zinc produced using the electro-thermic process is estimated from the percent of total secondary zinc production that this process accounted for during a single year, 2003. The amount of secondary zinc produced using the Waelz Kiln process is estimated from the percent of total secondary zinc production this process accounted for during a single year, 1997. This calculation could either overestimate or underestimate the percentage of the total secondary zinc production that is produced using the electro-thermic or Waelz Kiln processes. Therefore, there is uncertainty associated with the fact that percents of total production data estimated from production capacity, rather than actual production data, are used for emission estimates.

Second, there are uncertainties associated with the emission factors used to estimate CO₂ emissions from the primary and secondary production processes. Because the only published emission factors are based on the Imperial Smelting Furnace, which is not used in the United States, country-specific emission factors were developed for the Waelz Kiln zinc production process. Data limitations prevented the development of emission factors for the electro-thermic process. Therefore, emission factors for the Waelz Kiln process were applied to both electro-thermic and Waelz Kiln production processes. Furthermore, the Waelz Kiln emission factors are based on materials balances for metallurgical coke and EAF dust consumed during zinc production provided by Viklund-White (2000). Therefore, the accuracy of these emission factors depend upon the accuracy of these materials balances.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-45. Zinc production CO₂ emissions were estimated to be between 0.4 and 0.6 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 22 percent below and 25 percent above the emission estimate of 0.5 Tg CO₂ Eq.

Table 4-45: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Zinc Production (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Zinc Production	CO ₂	0.5	0.4	0.6	-22%	+25%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

The historical activity data used to calculate the emissions from zinc production were updated for the year 2004. The change resulted in a decrease of 0.03 Tg CO₂ Eq. (6 percent) in CO₂ emissions from zinc production for that year.

4.12. Lead Production (IPCC Source Category 2C5)

Lead production in the United States consists of both primary and secondary processes. In the United States, primary lead production, in the form of direct smelting, mostly occurs at a plants located in Alaska and Missouri, while secondary production largely involves the recycling of lead acid batteries at 14 separate smelters located in 11 states throughout the United States (USGS 2005). Secondary lead production has increased in the United States over the past decade while primary lead production has decreased. In 2005, secondary lead production accounted for approximately 89 percent of total lead production (Gabby 2006, USGS 1995). Both the primary lead and secondary lead production processes used in the United States emit CO₂ (Sjardin 2003).

Primary production of lead through the direct smelting of lead concentrate produces CO₂ emissions as the lead concentrates are reduced in a furnace using metallurgical coke (Sjardin 2003). U.S. primary lead production decreased by 3 percent from 2004 to 2005 and has decreased by 63 percent since 1990 (Gabby 2006, USGS 1995).

In the United States, approximately 82 percent of secondary lead is produced by recycling lead acid batteries in either blast furnaces or reverberatory furnaces. The remaining 18 percent of secondary lead is produced from lead scrap. Similar to primary lead production, CO₂ emissions result when a reducing agent, usually metallurgical coke, is added to the smelter to aid in the reduction process (Sjardin 2003). U.S. secondary lead production increased by 3 percent from 2004 to 2005, and has increased by 24 percent since 1990.

The United States is the third largest mine producer of lead in the world, behind China and Australia, accounting for 14 percent of world production in 2005 (USGS 2005). In 2005, U.S. primary and secondary lead production totaled 1,288,000 metric tons (Gabby 2006). The resulting emissions of CO₂ from 2005 production were estimated to be 0.3 Tg CO₂ Eq. (265 Gg) (see Table 4-46). The majority of 2005 lead production is from secondary processes, which account for 86 percent of total 2005 CO₂ emissions.

Table 4-46: CO₂ Emissions from Lead Production (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	0.3	285
1995	0.3	298
2000	0.3	311
2001	0.3	293

2002	0.3	290
2003	0.3	289
2004	0.3	259
2005	0.3	265

After a gradual increase in total emissions from 1990 to 2000, total emissions have decreased by seven percent since 1990, largely due a decrease in primary production and a transition within the United States from primary lead production to secondary lead production, which is less emissive than primary production (USGS 2005).

Methodology

Non-energy CO₂ emissions from lead production result from primary and secondary production processes that use metallurgical coke or other C-based materials as reductants. For primary lead production using direct smelting, Sjardin (2003) provides an emission factor of 0.25 metric tons CO₂/ton lead. For secondary lead production, Sjardin (2003) provides an emission factor of 0.2 metric tons CO₂/ton lead produced. Both factors are multiplied by total U.S. primary and secondary lead production, respectively, to estimate CO₂ emissions.

The 1990 through 2004 activity data for primary and secondary lead production (see Table 4-47) were obtained through the USGS *Mineral Yearbook: Lead* (USGS 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005). Primary and secondary lead production data for 2005 were obtained from the USGS Lead Minerals Commodity Specialist (Gabby 2006).

Table 4-47: Lead Production (Metric Tons)

Year	Primary	Secondary
1990	404,000	922,000
1995	374,000	1,020,000
2000	341,000	1,130,000
2001	290,000	1,100,000
2002	262,000	1,120,000
2003	245,000	1,140,000
2004	148,000	1,110,000
2005	143,000	1,145,000

Uncertainty

Uncertainty associated with lead production relates to the emission factors and activity data used. The direct smelting emission factor used in primary production is taken from Sjardin (2003) who averages the values provided by three other studies (Dutrillac et al. 2000, Morris et al. 1983, Ullman 1997). For secondary production, Sjardin (2003) reduces this factor by 50 percent and adds a CO₂ emissions factor associated with battery treatment. The applicability of these emission factors to plants in the United States is uncertain. There is also a smaller level of uncertainty associated with the accuracy of primary and secondary production data provided by the USGS.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-48. Lead production CO₂ emissions were estimated to be between 0.2 and 0.3 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 16 percent below and 17 percent above the emission estimate of 0.3 Tg CO₂ Eq.

Table 4-48: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Lead Production (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower	Upper	Lower	Upper

			Bound	Bound	Bound	Bound
Lead Production	CO ₂	0.3	0.2	0.3	-16%	+17%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

4.13. Petrochemical Production (IPCC Source Category 2B5)

The production of some petrochemicals results in the release of small amounts of CH₄ and CO₂ emissions. Petrochemicals are chemicals isolated or derived from petroleum or natural gas. CH₄ emissions are presented here from the production of C black, ethylene, ethylene dichloride, and methanol, while CO₂ emissions are presented here for only C black production. The CO₂ emissions from petrochemical processes other than C black are currently included in the Carbon Stored in Products from Non-Energy Uses of Fossil Fuels Section of the Energy chapter. The CO₂ from C black production is included here to allow for the direct reporting of CO₂ emissions from the process and direct accounting of the feedstocks used in the process.

C black is an intensely black powder generated by the incomplete combustion of an aromatic petroleum or coal-based feedstock. Most C black produced in the United States is added to rubber to impart strength and abrasion resistance, and the tire industry is by far the largest consumer. Ethylene is consumed in the production processes of the plastics industry including polymers such as high, low, and linear low density polyethylene (HDPE, LDPE, LLDPE), polyvinyl chloride (PVC), ethylene dichloride, ethylene oxide, and ethylbenzene. Ethylene dichloride is one of the first manufactured chlorinated hydrocarbons with reported production as early as 1795. In addition to being an important intermediate in the synthesis of chlorinated hydrocarbons, ethylene dichloride is used as an industrial solvent and as a fuel additive. Methanol is an alternative transportation fuel as well as a principle ingredient in windshield wiper fluid, paints, solvents, refrigerants, and disinfectants. In addition, methanol-based acetic acid is used in making PET plastics and polyester fibers.

Emissions of CO₂ and CH₄ from petrochemical production in 2005 were 2.9 Tg CO₂ Eq. (2,895 Gg) and 1.1 Tg CO₂ Eq. (52 Gg), respectively (see Table 4-49 and Table 4-50), totaling 4.0 Tg CO₂ Eq. Emissions of CO₂ from C black production in 2005 essentially equaled those from the previous year. There has been an overall increase in CO₂ emissions from C black production of 30 percent since 1990. CH₄ emissions from petrochemical production increased by six percent from the previous year and increased 26 percent since 1990.

Table 4-49: CO₂ and CH₄ Emissions from Petrochemical Production (Tg CO₂ Eq.)

Year	1990	1995	2000	2001	2002	2003	2004	2005
CO ₂	2.2	2.8	3.0	2.8	2.9	2.8	2.9	2.9
CH ₄	0.9	1.1	1.2	1.1	1.1	1.1	1.2	1.1
Total	3.1	3.8	4.2	3.9	4.0	3.9	4.1	4.0

Table 4-50: CO₂ and CH₄ Emissions from Petrochemical Production (Gg)

Year	1990	1995	2000	2001	2002	2003	2004	2005
CO ₂	2,221	2,750	3,004	2,787	2,857	2,777	2,895	2,897
CH ₄	41	52	58	51	52	51	55	51

Methodology

Emissions of CH₄ were calculated by multiplying annual estimates of chemical production by the appropriate emission factor, as follows: 11 kg CH₄/metric ton C black, 1 kg CH₄/metric ton ethylene, 0.4 kg CH₄/metric ton ethylene dichloride,¹⁰ and 2 kg CH₄/metric ton methanol. Although the production of other chemicals may also

¹⁰ The emission factor obtained from IPCC/UNEP/OECD/IEA (1997), page 2.23 is assumed to have a misprint; the chemical

result in CH₄ emissions, there were not sufficient data available to estimate their emissions.

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Annual production data for 1990 (see Table 4-51) were obtained from the Chemical Manufacturer's Association *Statistical Handbook* (CMA 1999). Production data for 1991 through 2005 were obtained from the American Chemistry Council's *Guide to the Business of Chemistry* (ACC 2002, 2003, 2005, 2006) and the International Carbon Black Association (Johnson 2003, 2005, 2006).

Table 4-51: Production of Selected Petrochemicals (Thousand Metric Tons)

Chemical	1990	1995	2000	2001	2002	2003	2004	2005
Carbon Black	1,307	1,619	1,769	1,641	1,682	1,635	1,705	1,651
Ethylene	16,542	21,215	24,971	22,521	23,623	22,957	25,660	23,955
Ethylene Dichloride	6,282	7,829	9,866	9,294	9,288	9,952	12,111	11,261
Methanol	3,785	4,992	4,876	3,402	3,289	3,166	2,937	2,336

Almost all C black in the United States is produced from petroleum-based or coal-based feedstocks using the "furnace black" process (European IPPC Bureau 2004). The furnace black process is a partial combustion process in which a portion of the C black feedstock is combusted to provide energy to the process. C black is also produced in the United States by the thermal cracking of acetylene-containing feedstocks ("acetylene black process") and by the thermal cracking of other hydrocarbons ("thermal black process"). One U.S. C black plant produces C black using the thermal black process, and one U.S. C black plant produces C black using the acetylene black process (The Innovation Group 2004).

The furnace black process produces C black from "C black feedstock" (also referred to as "C black oil"), which is a heavy aromatic oil that may be derived as a byproduct of either the petroleum refining process or the metallurgical (coal) coke production process. For the production of both petroleum-derived and coal-derived C black, the "primary feedstock" (i.e., C black feedstock) is injected into a furnace that is heated by a "secondary feedstock" (generally natural gas). Both the natural gas secondary feedstock and a portion of the C black feedstock are oxidized to provide heat to the production process and pyrolyze the remaining C black feedstock to C black. The "tail gas" from the furnace black process contains CO₂, carbon monoxide, sulfur compounds, CH₄, and non-CH₄ volatile organic compounds. A portion of the tail gas is generally burned for energy recovery to heat the downstream C black product dryers. The remaining tail gas may also be burned for energy recovery, flared, or vented uncontrolled to the atmosphere.

The calculation of the C lost during the production process is the basis for determining the amount of CO₂ released during the process. The C content of national C black production is subtracted from the total amount of C contained in primary and secondary C black feedstock to find the amount of C lost during the production process. It is assumed that the C lost in this process is emitted to the atmosphere as either CH₄ or CO₂. The C content of the CH₄ emissions, estimated as described above, is subtracted from the total C lost in the process to calculate the amount of C emitted as CO₂. The total amount of primary and secondary C black feedstock consumed in the process (see Table 4-52) is estimated using a primary feedstock consumption factor and a secondary feedstock consumption factor estimated from U.S. Census Bureau (1999 and 2004) data. The average C black feedstock consumption factor for U.S. C black production is 1.43 metric tons of C black feedstock consumed per metric ton of C black produced. The average natural gas consumption factor for U.S. C black production is 341 normal cubic meters of natural gas consumed per metric ton of C black produced. The amount of C contained in the primary and secondary feedstocks is calculated by applying the respective C contents of the feedstocks to the respective levels of feedstock consumption (EIA 2003, 2004).

Table 4-52: Carbon Black Feedstock (Primary Feedstock) and Natural Gas Feedstock (Secondary Feedstock) Consumption (Thousand Metric Tons)

identified should be ethylene dichloride (C₂H₄Cl₂) rather than dichloroethylene (C₂H₂Cl₂).

Activity	1990	1995	2000	2001	2002	2003	2004	2005
Primary Feedstock	1,864	2,308	2,521	2,339	2,398	2,331	2,430	2,430
Secondary Feedstock	302	374	408	379	388	377	393	393

For the purposes of emissions estimation, 100 percent of the primary C black feedstock is assumed to be derived from petroleum refining byproducts. C black feedstock derived from metallurgical (coal) coke production (e.g., creosote oil) is also used for C black production; however, no data are available concerning the annual consumption of coal-derived C black feedstock. C black feedstock derived from petroleum refining byproducts is assumed to be 89 percent elemental C (Srivastava et al. 1999). It is assumed that 100 percent of the tail gas produced from the C black production process is combusted and that none of the tail gas is vented to the atmosphere uncontrolled. The furnace black process is assumed to be the only process used for the production of C black because of the lack of data concerning the relatively small amount of C black produced using the acetylene black and thermal black processes. The C black produced from the furnace black process is assumed to be 97 percent elemental C (Othmer et al. 1992).

Uncertainty

The CH₄ emission factors used for petrochemical production are based on a limited number of studies. Using plant-specific factors instead of average factors could increase the accuracy of the emission estimates; however, such data were not available. There may also be other significant sources of CH₄ arising from petrochemical production activities that have not been included in these estimates.

The results of the quantitative uncertainty analysis for the CO₂ emissions from C black production calculation are based on feedstock consumption, import and export data, and C black production data. The composition of C black feedstock varies depending upon the specific refinery production process, and therefore the assumption that C black feedstock is 89 percent C gives rise to uncertainty. Also, no data are available concerning the consumption of coal-derived C black feedstock, so CO₂ emissions from the utilization of coal-based feedstock are not included in the emission estimate. In addition, other data sources indicate that the amount of petroleum-based feedstock used in C black production may be underreported by the U.S. Census Bureau. Finally, the amount of C black produced from the thermal black process and acetylene black process, although estimated to be a small percentage of the total production, is not known. Therefore, there is some uncertainty associated with the assumption that all of the C black is produced using the furnace black process.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-53. Petrochemical production CH₄ emissions were estimated to be between 1.0 and 1.2 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 8 percent below to 9 percent above the emission estimate of 1.1 Tg CO₂ Eq. Petrochemical production CO₂ emissions were estimated to be between 1.9 and 4.1 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 34 percent below to 41 percent above the emission estimate of 2.9 Tg CO₂ Eq.

Table 4-53: Tier 2 Quantitative Uncertainty Estimates for CH₄ Emissions from Petrochemical Production and CO₂ Emissions from Carbon Black Production (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission	Uncertainty Range Relative to Emission Estimate ^a			
		Estimate	(Tg CO ₂ Eq.)			
		(Tg CO ₂ Eq.)	Lower Bound	Upper Bound	Lower Bound	Upper Bound
Petrochemical Production	CO ₂	2.9	1.9	4.1	-34%	+41%
Petrochemical Production	CH ₄	1.1	1.0	1.2	-8%	+9%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

Estimates of CH₄ emissions from petrochemical production have been revised for the entire time series to include the removal of styrene, which has been removed due to inconsistent information regarding its emissive use in the

United States. On average, the removal of styrene resulted in a decrease of 0.4 Tg CO₂ Eq. (27 percent) from the previous estimate.

Planned Improvements

Future improvements to the petrochemicals source category include research into the use of acrylonitrile in the United States, revisions to the C black CH₄ and CO₂ emission factors, and research into process and feedstock data to obtain Tier 2 emission estimates from the production of methanol, ethylene, propylene, ethylene dichloride, and ethylene oxide.

4.14. Silicon Carbide Production (IPCC Source Category 2B4) and Consumption

CO₂ and CH₄ are emitted from the production of silicon carbide (SiC), a material used as an industrial abrasive. To make SiC, quartz (SiO₂) is reacted with C in the form of petroleum coke. A portion (about 35 percent) of the C contained in the petroleum coke is retained in the SiC. The remaining C is emitted as CO₂, CH₄, or CO.

CO₂ is also emitted from the consumption of SiC for metallurgical and other non-abrasive applications. The USGS reports that a portion (approximately 50 percent) of SiC is used in metallurgical and other non-abrasive applications, primarily in iron and steel production (USGS 2005a).

CO₂ from SiC production and consumption in 2005 were 219 Gg (0.2 Tg CO₂ Eq.). Approximately 42 percent of these emissions resulted from SiC production while the remainder result from SiC consumption. CH₄ emissions from SiC production in 2005 were 0.4 Gg CH₄ (0.01 Tg CO₂ Eq.) (see Table 4-54 and Table 4-55).

Table 4-54: CO₂ and CH₄ Emissions from Silicon Carbide Production and Consumption (Tg CO₂ Eq.)

Year	1990	1995	2000	2001	2002	2003	2004	2005
CO ₂	0.4	0.3	0.2	0.2	0.2	0.2	0.2	0.2
CH ₄	+	+	+	+	+	+	+	+
Total	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.2

+ Does not exceed 0.05 Tg CO₂ Eq.

Note: Totals may not sum due to independent rounding.

Table 4-55: CO₂ and CH₄ Emissions from Silicon Carbide Production and Consumption (Gg)

Year	1990	1995	2000	2001	2002	2003	2004	2005
CO ₂	375	329	248	199	183	202	224	219
CH ₄	1	1	1	+	+	+	+	+

+ Does not exceed 0.5 Gg.

Methodology

Emissions of CO₂ and CH₄ from the production of SiC were calculated by multiplying annual SiC production by the emission factors (2.62 metric tons CO₂/metric ton SiC for CO₂ and 11.6 kg CH₄/metric ton SiC for CH₄) provided by the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006).

Emissions of CO₂ were calculated by multiplying the annual SiC consumption (production plus net imports) by the percent used in metallurgical and other non-abrasive uses (50 percent) (USGS 2005a). The total SiC consumed in metallurgical and other non-abrasive uses was multiplied by the C content of SiC (31.5 percent), which was determined according to the molecular weight ratio of SiC.

Production data for 1990 through 2005 were obtained from the *Minerals Yearbook: Manufactured Abrasives* (USGS 1991a, 1992a, 1993a, 1994a, 1995a, 1996a, 1997a, 1998a, 1999a, 2000a, 2001a, 2002a, 2003a, 2004a, 2005a, 2006). Silicon carbide consumption by major end use was obtained from the *Minerals Yearbook: Silicon* (USGS 1991b, 1992b, 1993b, 1994b, 1995b, 1996b, 1997b, 1998b, 1999b, 2000b, 2001b, 2002b, 2003b, 2004b,

2005b) (see Table 4-56) for years 1990 through 2004 and from the USGS Minerals Commodity Specialist for 2005 (Corathers 2006). Net imports were obtained from the U.S. Census Bureau (2005, 2006).

Table 4-56: Production and Consumption of Silicon Carbide (Metric Tons)

Year	Production	Consumption
1990	105,000	172,464
1995	75,400	227,397
2000	45,000	225,280
2001	40,000	162,142
2002	30,000	180,956
2003	35,000	191,289
2004	35,000	229,692
2005	35,000	220,150

Uncertainty

There is uncertainty associated with the emission factors used because they are based on stoichiometry as opposed to monitoring of actual SiC production plants. An alternative would be to calculate emissions based on the quantity of petroleum coke used during the production process rather than on the amount of silicon carbide produced. However, these data were not available. For CH₄, there is also uncertainty associated with the hydrogen-containing volatile compounds in the petroleum coke (IPCC 2006). There is also some uncertainty associated with production, net imports, and consumption data as well as the percent of total consumption that is attributed to metallurgical and other non-abrasive uses.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-57. Silicon carbide production CH₄ emissions were estimated to be between 9 percent below and 9 percent above the emission estimate of 0.01 Tg CO₂ Eq. at the 95 percent confidence level. Silicon carbide production and consumption CO₂ emissions were estimated to be between 10 percent below and 10 percent above the emission estimate of 0.2 Tg CO₂ Eq. at the 95 percent confidence level.

Table 4-57: Tier 2 Quantitative Uncertainty Estimates for CH₄ and CO₂ Emissions from Silicon Carbide Production and Consumption (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission				
		Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Silicon Carbide Production and Consumption	CO ₂	0.2	0.2	0.2	-10%	+10%
Silicon Carbide Production and Consumption	CH ₄	+	+	+	-9%	+9%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

+ Does not exceed 0.05 Tg CO₂ Eq. or 0.5 Gg.

Recalculations Discussion

Emissions of CO₂ from SiC production were included for the first time during this inventory year. Overall emissions from CO₂ production and consumption increased throughout the time series by an average of 56 percent as a result of this change.

Planned Improvements

Future improvements to the carbide production source category include performing research to determine if calcium carbide production and consumption data are available for the United States. If these data are available, calcium carbide emission estimates will be included in this source category.

4.15. Nitric Acid Production (IPCC Source Category 2B2)

Nitric acid (HNO_3) is an inorganic compound used primarily to make synthetic commercial fertilizers. It is also a major component in the production of adipic acid—a feedstock for nylon—and explosives. Virtually all of the nitric acid produced in the United States is manufactured by the catalytic oxidation of ammonia (EPA 1997). During this reaction, N_2O is formed as a by-product and is released from reactor vents into the atmosphere.

Currently, the nitric acid industry controls for emissions of NO and NO_2 (i.e., NO_x). As such, the industry uses a combination of non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR) technologies. In the process of destroying NO_x , NSCR systems are also very effective at destroying N_2O . However, NSCR units are generally not preferred in modern plants because of high energy costs and associated high gas temperatures. NSCRs were widely installed in nitric plants built between 1971 and 1977. Approximately 20 percent of nitric acid plants use NSCR (Choe et al. 1993). The remaining 80 percent use SCR or extended absorption, neither of which is known to reduce N_2O emissions.

N_2O emissions from this source were estimated to be 15.7 Tg CO_2 Eq. (51 Gg) in 2005 (see Table 4-58). Emissions from nitric acid production have decreased by 12.1 percent since 1990, with the trend in the time series closely tracking the changes in production.

Table 4-58: N_2O Emissions from Nitric Acid Production (Tg CO_2 Eq. and Gg),

Year	Tg CO_2 Eq.	Gg
1990	17.8	58
1995	19.9	64
2000	19.6	63
2001	15.9	51
2002	17.2	56
2003	16.7	54
2004	16.0	52
2005	15.7	51

Methodology

N_2O emissions were calculated by multiplying nitric acid production by the amount of N_2O emitted per unit of nitric acid produced. The emission factor was determined as a weighted average of 2 kg N_2O / metric ton HNO_3 for plants using non-selective catalytic reduction (NSCR) systems and 9.5 kg N_2O /metric ton HNO_3 for plants not equipped with NSCR (Choe et al. 1993). In the process of destroying NO_x , NSCR systems destroy 80 to 90 percent of the N_2O , which is accounted for in the emission factor of 2 kg N_2O /metric ton HNO_3 . An estimated 20 percent of HNO_3 plants in the United States are equipped with NSCR (Choe et al. 1993). Hence, the emission factor is equal to $(9.5 \times 0.80) + (2 \times 0.20) = 8$ kg N_2O per metric ton HNO_3 .

Nitric acid production data for 1990 (see Table 4-59) was obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2001). Nitric acid production data for 1991 through 1992 (see Table 4-59) were obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2002). Nitric acid production data for 1993 was obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2004). Nitric acid production data for 1994 was obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2005). Nitric acid production data for 1995 through 2005 were obtained from *Chemical and Engineering News*, “Facts and Figures”

(C&EN 2006). The emission factor range was taken from Choe et al. (1993).

Table 4-59: Nitric Acid Production (Gg)

Year	Gg
1990	7,196
1995	8,018
2000	7,898
2001	6,416
2002	6,940
2003	6,747
2004	6,466
2005	6,328

Uncertainty

The overall uncertainty associated with the 2005 N₂O emissions estimate from nitric acid production was calculated using the IPCC *Good Practice Guidance* Tier 2 methodology. Uncertainty associated with the parameters used to estimate N₂O emissions included that of production data, the share of U.S. nitric acid production attributable to each emission abatement technology, and the emission factors applied to each abatement technology type.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-60. N₂O emissions from nitric acid production were estimated to be between 13.2 and 18.5 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 16 percent below to 18 percent above the 2005 emissions estimate of 15.7 Tg CO₂ Eq.

Table 4-60: Tier 2 Quantitative Uncertainty Estimates for N₂O Emissions From Nitric Acid Production (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Nitric Acid Production	N ₂ O	15.7	13.2	18.5	-16%	+18%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

The nitric acid production values for 1998, 2002, and 2004 have been updated relative to the previous Inventory based on revised production data presented in C&EN (2006). The updated production data for 1998 and 2002 resulted in an increases of less than 0.01Tg CO₂ Eq. (0.01 percent), respectively, in N₂O emissions from nitric acid production for these years relative to the previous Inventory. The updated production data for 2004 resulted in a decrease of 0.6 Tg CO₂ Eq. (3.5 percent) in N₂O emissions relative to the previous Inventory.

Planned Improvements

Planned improvements are focused on assessing the plant-by-plant implementation of NO_x abatement technologies to more accurately match plant production capacities to appropriate emission factors, instead of using a national profiling of abatement implementation.

4.16. Adipic Acid Production (IPCC Source Category 2B3)

Adipic acid production is an anthropogenic source of N₂O emissions. Worldwide, few adipic acid plants exist. The

United States is the major producer, with three companies in four locations accounting for approximately one-third of world production (CW 2005). Adipic acid is a white crystalline solid used in the manufacture of synthetic fibers, coatings, plastics, urethane foams, elastomers, and synthetic lubricants. Commercially, it is the most important of the aliphatic dicarboxylic acids, which are used to manufacture polyesters. Approximately 90 percent of all adipic acid produced in the United States is used in the production of nylon 6,6 (CMR 2001). Food grade adipic acid is also used to provide some foods with a “tangy” flavor (Thiemens and Trogler 1991).

Adipic acid is produced through a two-stage process during which N_2O is generated in the second stage. The first stage of manufacturing usually involves the oxidation of cyclohexane to form a cyclohexanone/cyclohexanol mixture. The second stage involves oxidizing this mixture with nitric acid to produce adipic acid. N_2O is generated as a by-product of the nitric acid oxidation stage and is emitted in the waste gas stream (Thiemens and Trogler 1991). Process emissions from the production of adipic acid vary with the types of technologies and level of emission controls employed by a facility. In 1990, two of the three major adipic acid-producing plants had N_2O abatement technologies in place and, as of 1998, the three major adipic acid production facilities had control systems in place.¹¹ Only one small plant, representing approximately two percent of production, does not control for N_2O (Reimer 1999).

N_2O emissions from adipic acid production were estimated to be 6.0 Tg CO_2 Eq. (19 Gg) in 2005 (see Table 4-61). National adipic acid production has increased by approximately 42 percent over the period of 1990 through 2005, to approximately one million metric tons. At the same time, emissions have been reduced by 61 percent due to the widespread installation of pollution control measures.

Table 4-61: N_2O Emissions from Adipic Acid Production (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	15.2	49
1995	17.2	56
2000	6.0	19
2001	4.9	16
2002	5.9	19
2003	6.2	20
2004	5.7	19
2005	6.0	19

Methodology

For two production plants, 1990 to 2002 emission estimates were obtained directly from the plant engineer and account for reductions due to control systems in place at these plants during the time series (Childs 2002, 2003). These estimates were based on continuous emissions monitoring equipment installed at the two facilities. Reported estimates for 2003, 2004, and 2005 were unavailable and, thus, were calculated by applying a 4.4, 4.2 and 4.2 percent production growth rates, respectively. The production for 2003 was obtained through linear interpolation between 2002 and 2004 reported national production data. Subsequently, the growth rate for 2004 and 2005 was based on the change between the estimated 2003 production data and the reported 2004 production data (see discussion below on sources of production data). For the other two plants, N_2O emissions were calculated by multiplying adipic acid production by an emission factor (i.e., N_2O emitted per unit of adipic acid produced) and adjusting for the percentage of N_2O released as a result of plant-specific emission controls. On the basis of experiments, the overall reaction stoichiometry for N_2O production in the preparation of adipic acid was estimated at approximately 0.3 metric tons of N_2O per metric ton of product (Thiemens and Trogler 1991). Emissions are

¹¹During 1997, the N_2O emission controls installed by the third plant operated for approximately a quarter of the year.

estimated using the following equation:

$$\text{N}_2\text{O emissions} = (\text{production of adipic acid [metric tons \{MT\} of adipic acid]}) \times (0.3 \text{ MT N}_2\text{O} / \text{MT adipic acid}) \times (1 - [\text{N}_2\text{O destruction factor} \times \text{abatement system utility factor}])$$

The “N₂O destruction factor” represents the percentage of N₂O emissions that are destroyed by the installed abatement technology. The “abatement system utility factor” represents the percentage of time that the abatement equipment operates during the annual production period. Overall, in the United States, two of the plants employ catalytic destruction, one plant employs thermal destruction, and the smallest plant uses no N₂O abatement equipment. The N₂O abatement system destruction factor is assumed to be 95 percent for catalytic abatement and 98 percent for thermal abatement (Reimer et al. 1999, Reimer 1999). For the one plant that uses thermal destruction and for which no reported plant-specific emissions are available, the abatement system utility factor is assumed to be 98 percent.

For 1990 to 2003 and 2005, plant-specific production data was estimated where direct emission measurements were not available. In order to calculate plant-specific production for the two plants, national adipic acid production was allocated to the plant level using the ratio of their known plant capacities to total national capacity for all U.S. plants. The estimated plant production for the two plants was then used for calculating emissions as described above. For 2004, actual plant production data were obtained for these two plants and used for emission calculations.

National adipic acid production data (see Table 4-62) for 1990 through 2002 were obtained from the American Chemistry Council (ACC 2003). Production for 2003 was estimated based on linear interpolation of 2002 and 2004 reported production. Production for 2004 was obtained from *Chemical Week*, Product Focus: Adipic Acid (CW 2005). Production for 2005 was calculated by applying a 4.2 percent production growth rate to reported 2004 production. This growth rate was based on the change between the estimated 2003 production and the reported 2004 production. The 4.2 percent production growth rate applied in this case is in line with the expected growth in global adipic acid demand of 3.2 percent per year from 2005 to 2010 (CW 2005). Plant capacities for 1990 through 1994 were obtained from *Chemical and Engineering News*, “Facts and Figures” and “Production of Top 50 Chemicals” (C&EN 1992, 1993, 1994, 1995). Plant capacities for 1995 and 1996 were kept the same as 1994 data. The 1997 plant capacities were taken from *Chemical Market Reporter* “Chemical Profile: Adipic Acid” (CMR 1998). The 1998 plant capacities for all four plants and 1999 plant capacities for three of the plants were obtained from *Chemical Week*, Product Focus: Adipic Acid/Adiponitrile (CW 1999). Plant capacities for 2000 for three of the plants were updated using *Chemical Market Reporter*, “Chemical Profile: Adipic Acid” (CMR 2001). For 2001 through 2005, the plant capacities for these three plants were kept the same as the year 2000 capacities. Plant capacity for 1999 to 2005 for the one remaining plant was kept the same as 1998.

Table 4-62: Adipic Acid Production (Gg)

Year	Gg
1990	735
1995	830
2000	925
2001	835
2002	921
2003	961
2004	1,002
2005	1,044

Uncertainty

The overall uncertainty associated with the 2005 N₂O emission estimate from adipic acid production was calculated using the IPCC *Good Practice Guidance* Tier 2 methodology. Uncertainty associated with the parameters used to estimate N₂O emissions included that of company specific production data, industry wide estimated production growth rates, emission factors for abated

and unabated emissions, and company specific historical emissions estimates.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-63. N₂O emissions from adipic acid production were estimated to be between 3.2 and 8.8 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 46 percent below to 47 percent above the 2005 emission estimate of 6.0 Tg CO₂ Eq.

Table 4-63: Tier 2 Quantitative Uncertainty Estimates for N₂O Emissions from Adipic Acid Production (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Adipic Acid Production	N ₂ O	6.0	3.2	8.8	-46%	+47%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Planned Improvements

Improvement efforts will be focused on obtaining direct measurement data from facilities. If they become available, cross verification with top-down approaches will provide a useful Tier 2 level QC check. Also, additional information on the actual performance of the latest catalytic and thermal abatement equipment at plants with continuous emission monitoring may support the re-evaluation of current default abatement values.

4.17. Substitution of Ozone Depleting Substances (IPCC Source Category 2F)

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are used as alternatives to several classes of ozone-depleting substances (ODSs) that are being phased out under the terms of the *Montreal Protocol* and the Clean Air Act Amendments of 1990.¹² Ozone depleting substances—chlorofluorocarbons (CFCs), halons, carbon tetrachloride, methyl chloroform, and hydrochlorofluorocarbons (HCFCs)—are used in a variety of industrial applications including refrigeration and air conditioning equipment, solvent cleaning, foam production, sterilization, fire extinguishing, and aerosols. Although HFCs and PFCs, are not harmful to the stratospheric ozone layer, they are potent greenhouse gases. Emission estimates for HFCs and PFCs used as substitutes for ODSs are provided in Table 4-64 and Table 4-65.

Table 4-64: Emissions of HFCs and PFCs from ODS Substitutes (Tg CO₂ Eq.)

Gas	1990	1995	2000	2001	2002	2003	2004	2005
HFC-23	+	+	+	+	+	+	+	+
HFC-32	+	+	0.3	0.3	0.4	0.4	0.5	0.6
HFC-125	+	3.5	11.2	12.4	13.7	15.4	17.3	19.8
HFC-134a	+	26.0	56.3	60.7	64.7	68.3	71.8	74.0
HFC-143a	+	0.9	8.3	10.3	12.7	15.4	18.4	22.1
HFC-236fa	+	0.2	0.7	0.8	0.8	0.9	1.0	1.0
CF ₄	+	+	+	+	+	+	+	+
Others*	0.3	1.6	4.2	4.0	4.5	5.1	5.4	5.7
Total	0.3	32.2	80.9	88.6	96.9	105.5	114.5	123.3

+ Does not exceed 0.05 Tg CO₂ Eq.

* Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee, and PFC/PFPEs, the latter being a proxy for a diverse

¹² [42 U.S.C § 7671, CAA § 601]

collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications. For estimating purposes, the GWP value used for PFC/PFPEs was based upon C_6F_{14} .

Note: Totals may not sum due to independent rounding.

Table 4-65: Emissions of HFCs and PFCs from ODS Substitution (Mg)

Gas	1990	1995	2000	2001	2002	2003	2004	2005
HFC-23	+	+	1	2	2	2	3	3
HFC-32	+	+	465	498	558	645	762	963
HFC-125	+	1,267	3,983	4,423	4,901	5,484	6,177	7,065
HFC-134a	+	19,999	43,274	46,677	49,774	52,521	55,265	56,943
HFC-143a	+	228	2,193	2,723	3,338	4,045	4,847	5,822
HFC-236fa	+	36	110	123	135	145	155	163
CF ₄	+	+	1	1	1	1	1	2
Others*	M	M	M	M	M	M	M	M

M (Mixture of Gases)

+ Does not exceed 0.5 Mg

* Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee, C₄F₁₀, and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications.

In 1990 and 1991, the only significant emissions of HFCs and PFCs as substitutes to ODSs were relatively small amounts of HFC-152a—a component of the refrigerant blend R-500 used in chillers—and HFC-134a in refrigeration end-uses. Beginning in 1992, HFC-134a was used in growing amounts as a refrigerant in motor vehicle air-conditioners and in refrigerant blends such as R-404A.¹³ In 1993, the use of HFCs in foam production and as an aerosol propellant began, and in 1994 these compounds also found applications as solvents and sterilants. In 1995, ODS substitutes for halons entered widespread use in the United States as halon production was phased-out.

The use and subsequent emissions of HFCs and PFCs as ODS substitutes has been increasing from small amounts in 1990 to 123.3 Tg CO₂ Eq. in 2005. This increase was in large part the result of efforts to phase out CFCs and other ODSs in the United States. In the short term, this trend is expected to continue, and will likely accelerate over the next decade as HCFCs, which are interim substitutes in many applications, are themselves phased-out under the provisions of the Copenhagen Amendments to the *Montreal Protocol*. Improvements in the technologies associated with the use of these gases and the introduction of alternative gases and technologies, however, may help to offset this anticipated increase in emissions.

The end-use sectors that contribute the most toward emissions of HFCs and PFCs as ODS substitutes include refrigeration and air-conditioning (107.8 Tg CO₂ Eq., or approximately 87 percent), aerosols (11.3 Tg CO₂ Eq., or approximately 9 percent), and solvents (1.6 Tg CO₂ Eq., or approximately 1 percent). Within the refrigeration and air-conditioning end-use sector, motor vehicle air-conditioning was the highest emitting end-use (53.1 Tg CO₂ Eq.), followed by retail food and refrigerated transport. In the aerosols end-use sector, non-metered-dose inhaler (MDI) emissions make up a majority of the end-use sector emissions.

Methodology

A detailed Vintaging Model of ODS-containing equipment and products was used to estimate the actual—versus potential—emissions of various ODS substitutes, including HFCs and PFCs. The name of the model refers to the fact that the model tracks the use and emissions of various compounds for the annual “vintages” of new equipment that enter service in each end-use. This Vintaging Model predicts ODS and ODS substitute use in the United States based on modeled estimates of the quantity of equipment or products sold each year containing these chemicals and the amount of the chemical required to manufacture and/or maintain equipment and products over time. Emissions

¹³ R-404A contains HFC-125, HFC-143a, and HFC-134a.

for each end-use were estimated by applying annual leak rates and release profiles, which account for the lag in emissions from equipment as they leak over time. By aggregating the data for more than 50 different end-uses, the model produces estimates of annual use and emissions of each compound. Further information on the Vintaging Model is contained in Annex 3.8.

Uncertainty

Given that emissions of ODS substitutes occur from thousands of different kinds of equipment and from millions of point and mobile sources throughout the United States, emission estimates must be made using analytical tools such as the Vintaging Model or the methods outlined in IPCC/UNEP/OECD/IEA (1997). Though the model is more comprehensive than the IPCC default methodology, significant uncertainties still exist with regard to the levels of equipment sales, equipment characteristics, and end-use emissions profiles that were used to estimate annual emissions for the various compounds.

The Vintaging Model estimates emissions from over 50 end-uses. The uncertainty analysis, however, quantifies the level of uncertainty associated with the aggregate emissions resulting from the top 16 end-uses and 5 others. In an effort to improve the uncertainty analysis, additional end-uses are added annually, with the intention that over time uncertainty for all emissions from the Vintaging Model will be fully characterized. This year, one new end-use was included in the uncertainty estimate- fire extinguishing streaming agents. Any end-uses included in previous years' uncertainty analysis were included in the current uncertainty analysis, whether or not those end-uses were included in the top 95 percent of emissions from ODS Substitutes.

In order to calculate uncertainty, functional forms were developed to simplify some of the complex "vintaging" aspects of some end-use sectors, especially with respect to refrigeration and air-conditioning, and to a lesser degree, fire extinguishing. These sectors calculate emissions based on the entire lifetime of equipment, not just equipment put into commission in the current year, thereby necessitating simplifying equations. The functional forms used variables that included growth rates, emission factors, transition from ODSs, change in charge size as a result of the transition, disposal quantities, disposal emission rates, and either stock for the current year or original ODS consumption. Uncertainty was estimated around each variable within the functional forms based on expert judgment, and a Monte Carlo analysis was performed. The most significant sources of uncertainty for this source category include the emission factors for mobile air-conditioning and retail food refrigeration, as well as the stock (MT) of retail food refrigerant.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-66. Substitution of ozone depleting substances HFC and PFC emissions were estimated to be between 95.0 and 158.9 Tg CO₂ Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 9 percent below to 13 percent above the emission estimate of 123.3 Tg CO₂ Eq.

Table 4-66: Tier 2 Quantitative Uncertainty Estimates for HFC and PFC Emissions from ODS Substitutes (Tg CO₂ Eq. and Percent)

Source	Gases	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a (Tg CO ₂ Eq.)			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Substitution of Ozone Depleting Substances	HFCs and PFCs	123.3	112.7	148.6	-9%	+20%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

An extensive review of the chemical substitution trends, market sizes, growth rates, and charge sizes, together with input from industry representatives, resulted in updated assumptions for the Vintaging Model. These changes resulted in an average annual net increase of 7.6 Tg CO₂ Eq. (21 percent) in HFC and PFC emissions from the substitution of ozone depleting substances for the period 1990 through 2004.

4.18. HCFC-22 Production (IPCC Source Category 2E1)

Trifluoromethane (HFC-23 or CHF₃) is generated as a by-product during the manufacture of chlorodifluoromethane (HCFC-22), which is primarily employed in refrigeration and air conditioning systems and as a chemical feedstock for manufacturing synthetic polymers. Between 1990 and 2000, U.S. production of HCFC-22 increased significantly as HCFC-22 replaced chlorofluorocarbons (CFCs) in many applications. Since 2000, U.S. production has fluctuated. Because HCFC-22 depletes stratospheric ozone, its production for non-feedstock uses is scheduled to be phased out by 2020 under the U.S. Clean Air Act.¹⁴ Feedstock production, however, is permitted to continue indefinitely.

HCFC-22 is produced by the reaction of chloroform (CHCl₃) and hydrogen fluoride (HF) in the presence of a catalyst, SbCl₅. The reaction of the catalyst and HF produces SbCl_xF_y, (where x + y = 5), which reacts with chlorinated hydrocarbons to replace chlorine atoms with fluorine. The HF and chloroform are introduced by submerged piping into a continuous-flow reactor that contains the catalyst in a hydrocarbon mixture of chloroform and partially fluorinated intermediates. The vapors leaving the reactor contain HCFC-21 (CHCl₂F), HCFC-22 (CHClF₂), HFC-23 (CHF₃), HCl, chloroform, and HF. The under-fluorinated intermediates (HCFC-21) and chloroform are then condensed and returned to the reactor, along with residual catalyst, to undergo further fluorination. The final vapors leaving the condenser are primarily HCFC-22, HFC-23, HCl and residual HF. The HCl is recovered as a useful byproduct, and the HF is removed. Once separated from HCFC-22, the HFC-23 is generally vented to the atmosphere as an unwanted by-product, but it is sometimes captured for use in a limited number of applications.

Emissions of HFC-23 in 2005 were estimated to be 16.5 Tg CO₂ Eq. (1.3 Gg) (Table 4-67). This quantity represents a 6 percent increase from 2004 emissions and a 53 percent decline from 1990 emissions. The increase in 2005 emissions is due primarily to a slight increase in the HFC-23 emission rate (i.e., the amount of HFC-23 emitted per kilogram of HCFC-22 manufactured), while the decline from 1990 emissions is primarily due to the large decline in the HFC-23 emission rate between 1990 and 2005. Three HCFC-22 production plants operated in the United States in 2005, two of which used thermal oxidation to significantly lower their HFC-23 emissions.

Table 4-67: HFC-23 Emissions from HCFC-22 Production (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	35.0	3
1995	27.0	2
2000	29.8	3
2001	19.8	2
2002	19.8	2
2003	12.3	1
2004	15.6	1
2005	16.5	1

Methodology

The methodology employed for estimating emissions is based upon measurements at individual HCFC-22 production plants. Plants using thermal oxidation to abate their HFC-23 emissions monitor the performance of their oxidizers to verify that the HFC-23 is almost completely destroyed. The other plants periodically measure HFC-23 concentrations in the output stream using gas chromatography. This information is combined with information on

¹⁴ As construed, interpreted, and applied in the terms and conditions of the *Montreal Protocol on Substances that Deplete the Ozone Layer*. [42 U.S.C. §7671m(b), CAA §614]

quantities of critical feed components (e.g., HF) and/or products (HCFC-22) to estimate HFC-23 emissions using a material balance approach. HFC-23 concentrations are determined at the point the gas leaves the chemical reactor; therefore, estimates also include fugitive emissions.

Production data and emission estimates were prepared in cooperation with the U.S. manufacturers of HCFC-22 (ARAP 1997, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006; RTI 1997). Annual estimates of U.S. HCFC-22 production are presented in Table 4-68.

Table 4-68: HCFC-22 Production (Gg)

Year	Gg
1990	139
1995	155
2000	187
2001	152
2002	144
2003	138
2004	155
2005	156

Uncertainty

A high level of confidence has been attributed to the HFC-23 concentration data employed because measurements were conducted frequently and accounted for day-to-day and process variability. The results of the Tier 1 quantitative uncertainty analysis are summarized in Table 4-69. HFC-23 emissions from HCFC-22 production were estimated to be between 14.9 and 18.2 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of 10 percent above and 10 percent below the 2005 emission estimate of 16.5 Tg CO₂ Eq.

Table 4-69: Tier 1 Quantitative Uncertainty Estimates for HFC-23 Emissions from HCFC-22 Production (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			Lower Bound		Upper Bound	
HCFC-22 Production	HFC-23	16.5	14.9	18.2	-10%	+10%

^a Range of emission reflect a 95 percent confidence interval.

4.19. Electrical Transmission and Distribution (IPCC Source Category 2F7)

The largest use of SF₆, both in the United States and internationally, is as an electrical insulator and interrupter in equipment that transmits and distributes electricity (RAND 2004). The gas has been employed by the electric power industry in the United States since the 1950s because of its dielectric strength and arc-quenching characteristics. It is used in gas-insulated substations, circuit breakers, and other switchgear. Sulfur hexafluoride has replaced flammable insulating oils in many applications and allows for more compact substations in dense urban areas.

Fugitive emissions of SF₆ can escape from gas-insulated substations and switch gear through seals, especially from older equipment. The gas can also be released during equipment manufacturing, installation, servicing, and disposal. Emissions of SF₆ from equipment manufacturing and from electrical transmission and distribution systems were estimated to be 13.2 Tg CO₂ Eq. (0.6 Gg) in 2005. This quantity represents a 51 percent decrease from the estimate for 1990 (see Table 4-70 and Table 4-71). This decrease is believed to be a response to increases

in the price of SF₆ during the 1990s and to growing awareness of the environmental impact of SF₆ emissions, through programs such as the EPA's SF₆ Emission Reduction Partnership for Electric Power Systems.

Table 4-70: SF₆ Emissions from Electric Power Systems and Electrical Equipment Manufacturers (Tg CO₂ Eq.)

Year	Electric Power Systems	Electrical Equipment Manufacturers	Total
1990	26.8	0.3	27.1
1995	21.3	0.5	21.8
2000	14.5	0.7	15.2
2001	14.4	0.7	15.1
2002	13.7	0.7	14.3
2003	13.2	0.7	13.8
2004	12.9	0.7	13.6
2005	12.5	0.7	13.2

Table 4-71: SF₆ Emissions from Electric Power Systems and Electrical Equipment Manufacturers (Gg)

Year	Emissions
1990	1.1
1995	0.9
2000	0.6
2001	0.6
2002	0.6
2003	0.6
2004	0.6
2005	0.6

Methodology

The estimates of emissions from electric transmission and distribution are comprised of emissions from electric power systems and emissions from the manufacture of electrical equipment. The methodologies for estimating both sets of emissions are described below.

1999 to 2005 Emissions from Electric Power Systems

Emissions from electric power systems from 1999 to 2005 were estimated based on: (1) reporting from utilities participating in EPA's SF₆ Emission Reduction Partnership for Electric Power Systems (partners), which began in 1999; and, (2) utilities' transmission miles as reported in the 2001 and 2004 Utility Data Institute (UDI) Directories of Electric Power Producers and Distributors (UDI 2001, 2004). (Transmission miles are defined as the miles of lines carrying voltages above 34.5 kV.) Over the period from 1999 to 2005, participating utilities represented between 31 percent and 39 percent of total U.S. transmission miles. For each year, the emissions reported by participating utilities were added to the emissions estimated for utilities that do not participate in the Partnership (i.e., non-partners).

Emissions from partner utilities were estimated using a combination of reported data and, where reported data were unavailable, interpolated or extrapolated data. If a partner utility did not provide data for a historical year, emissions were interpolated between years for which data were available. For 2005, if no data was provided, estimates were calculated based on historical trends or partner-specific emission reduction targets (i.e., emissions were assumed to decline linearly toward a partners' future stated goal). In 2005, non-reporting partners account for approximately 2 percent of the total emissions attributable to utilities involved in the SF₆ Emission Reduction Partnership.

Emissions from non-partners in every year since 1999 were estimated using the results of a regression analysis that showed that the emissions of reporting utilities were most strongly correlated with their transmission miles. The results of this analysis are not surprising given that, in the United States, SF₆ is contained primarily in transmission equipment rated at or above 34.5 kV. The equations were developed based on the 1999 SF₆ emissions reported by 49 partner utilities (representing approximately 31 percent of U.S. transmission miles), and 2000 transmission mileage data obtained from the 2001 UDI Directory of Electric Power Producers and Distributors (UDI 2001). Two equations were developed, one for small and one for large utilities (i.e., with less or more than 10,000 transmission miles, respectively). The distinction between utility sizes was made because the regression analysis showed that the relationship between emissions and transmission miles differed for small and large transmission networks. The same equations were used to estimate non-partner emissions in 1999 and every year thereafter because non-partners were assumed not to have implemented any changes that would have resulted in reduced emissions since 1999.

The regression equations are:

Non-partner small utilities (less than 10,000 transmission miles, in kilograms):

$$\text{Emissions (kg)} = 0.874 \times \text{Transmission Miles}$$

Non-partner large utilities (more than 10,000 transmission miles, in kilograms):

$$\text{Emissions (kg)} = 0.558 \times \text{Transmission Miles}$$

Data on transmission miles for each non-partner utility for the years 2000 and 2003 were obtained from the 2001 and 2004 UDI Directories of Electric Power Producers and Distributors, respectively (UDI 2001, 2004). Given that the U.S. transmission system grew by over 14,000 miles between 2000 and 2003, and that this increase probably occurred gradually, transmission mileage was assumed to increase exponentially at an annual rate of 0.7 percent between 2000 and 2003. This growth rate is assumed to have continued through 2005.

As a final step, total emissions were determined for each year by summing the partner emissions (reported to the EPA's SF₆ Emission Reduction Partnership for Electric Power Systems), and the non-partner emissions (determined using the 1999 regression equation).

1990 to 1998 Emissions from Electric Power Systems

Because most participating utilities reported emissions only for 1999 through 2005, it was necessary to model SF₆ emissions from electric power systems for the years 1990 through 1998. To do so, it was assumed that U.S. emissions followed the same trajectory as global emissions from this source during the 1990 to 1998 period. To estimate global emissions, the RAND survey of global SF₆ sales were used, together with the following equation, which is derived from the mass-balance equation for chemical emissions (Volume 3, Equation 7.3) in the IPCC *Guidelines for National Greenhouse Gas Inventories* (IPCC 2006). (Although equation 7.3 of the IPCC Guidelines appears in the discussion of substitutes for ozone-depleting substances, it is applicable to emissions from any long-lived pressurized equipment that is periodically serviced during its lifetime.)

$$\text{Emissions (kilograms)} = \text{SF}_6 \text{ purchased to refill existing equipment (kilograms)} + \text{nameplate capacity of retiring equipment (kilograms)}$$

Note that the above equation holds whether the gas from retiring equipment is released or recaptured; if the gas is recaptured, it is used to refill existing equipment, thereby lowering the amount of SF₆ purchased by utilities for this purpose.

Sulfur hexafluoride purchased to refill existing equipment in a given year was assumed to be approximately equal to the SF₆ purchased by utilities in that year. Gas purchases by utilities and equipment manufacturers from 1961 through 2003 are available from the RAND (2004) survey. To estimate the quantity of SF₆ released or recovered from retiring equipment, the nameplate capacity of retiring equipment in a given year was assumed to equal 81.2 percent of the amount of gas purchased by electrical equipment manufacturers 40 years previous (e.g., in 2000, the

nameplate capacity of retiring equipment was assumed to equal 81.2 percent of the gas purchased in 1960). The remaining 18.8 percent was assumed to have been emitted at the time of manufacture. The 18.8 percent emission factor is an average of IPCC default SF₆ emission rates for Europe and Japan for 1995 (IPCC 2006). The 40-year lifetime for electrical equipment is also based on IPCC (2006). The results of the two components of the above equation were then summed to yield estimates of global SF₆ emissions from 1990 through 1998.

U.S. emissions between 1990 and 1998 are assumed to follow the same trajectory as global emissions during this period. To estimate U.S. emissions, global emissions for each year from 1990 through 1998 were divided by the estimated global emissions from 1999. The result was a time series of factors that express each year's global emissions as a multiple of 1999 global emissions. Historical U.S. emissions were estimated by multiplying the factor for each respective year by the estimated U.S. emissions of SF₆ from electric power systems in 1999 (estimated to be 15.3 Tg CO₂ Eq.).

Two factors may affect the relationship between the RAND sales trends and actual global emission trends. One is utilities' inventories of SF₆ in storage containers. When SF₆ prices rise, utilities are likely to deplete internal inventories before purchasing new SF₆ at the higher price, in which case SF₆ sales will fall more quickly than emissions. On the other hand, when SF₆ prices fall, utilities are likely to purchase more SF₆ to rebuild inventories, in which case sales will rise more quickly than emissions. This effect was accounted for by applying 3-year smoothing to utility SF₆ sales data. The other factor that may affect the relationship between the RAND sales trends and actual global emissions is the level of imports from and exports to Russia and China. SF₆ production in these countries is not included in the RAND survey, but may have been significant during the 1990 through 1999 period. This factor was not accounted for; however, atmospheric studies confirmed that the downward trend in the estimated global emissions between 1995 and 1998 was real (see the Uncertainty discussion below).

1990 to 2005 Emissions from Manufacture of Electrical Equipment

The 1990 to 2005 emissions estimates for original equipment manufacturers (OEMs) were derived by assuming that manufacturing emissions equal 10 percent of the quantity of SF₆ charged into new equipment. The quantity of SF₆ charged into new equipment was estimated based on statistics compiled by the National Electrical Manufacturers Association (NEMA). These statistics were provided for 1990 to 2000; the quantities of SF₆ charged into new equipment for 2001 to 2005 were assumed to equal that charged into equipment in 2000. The 10 percent emission rate is the average of the "ideal" and "realistic" manufacturing emission rates (4 percent and 17 percent, respectively) identified in a paper prepared under the auspices of the International Council on Large Electric Systems (CIGRE) in February 2002 (O'Connell et al. 2002).

Uncertainty

To estimate the uncertainty associated with emissions of SF₆ from electric transmission and distribution, uncertainties associated with three variables were estimated: (1) emissions from partners, (2) emissions from non-partners, and (3) emissions from manufacturers of electrical equipment. A Monte Carlo analysis was then applied to estimate the overall uncertainty of the emissions estimate.

Total emissions from the SF₆ Emission Reduction Partnership include emissions from both reporting and non-reporting partners. For reporting partners, individual partner-reported SF₆ data was assumed to have an uncertainty of 10 percent. Based on a Monte Carlo analysis, the cumulative uncertainty of all partner reported data was estimated to be 4.9 percent. The uncertainty associated with extrapolated or interpolated emissions from non-reporting partners was assumed to be 20 percent.

There are two sources of uncertainty associated with the regression equations used to estimate emissions in 2005 from non-partners: 1) uncertainty in the coefficients (as defined by the regression standard error estimate), and 2) the uncertainty in total transmission miles for non-partners. In addition, there is uncertainty associated with the assumption that the emission factor used for non-partner utilities (which accounted for approximately 61 percent of U.S. transmission miles) will remain at levels defined by partners who reported in 1999. However, the last source of uncertainty was not modeled.

Uncertainties were also estimated regarding the quantity of SF₆ charged into equipment by equipment manufacturers, which is projected from 2000 data from NEMA, and the manufacturers' SF₆ emissions rate

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-72. Electrical Transmission and Distribution SF₆ emissions were estimated to be between 12.4 and 14.1 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 6 percent below and 7 percent above the emission estimate of 13.2 Tg CO₂ Eq.

Table 4-72: Tier 2 Quantitative Uncertainty Estimates for SF₆ Emissions from Electrical Transmission and Distribution (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to 2005 Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Electrical Transmission and Distribution	SF ₆	13.2	12.4	14.1	-6%	+7%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

In addition to the uncertainty quantified above, there is uncertainty associated with using global SF₆ sales data to estimate U.S. emission trends from 1990 through 1999. However, the trend in global emissions implied by sales of SF₆ appears to reflect the trend in global emissions implied by changing SF₆ concentrations in the atmosphere. That is, emissions based on global sales declined by 29 percent between 1995 and 1998, and emissions based on atmospheric measurements declined by 27 percent over the same period. However, U.S. emission patterns may differ from global emission patterns.

Recalculations Discussion

Relative to the previous Inventory report, SF₆ emission estimates for the period 1990 through 2004 were updated based on 1) new data from EPA's SF₆ Emission Reduction Partnership, and 2) revisions to the assumptions used in estimating global emissions between 1990 and 1999. For the period 1999 through 2004, estimates have been revised to incorporate additional data from new partners. For the period 1990 through 1998, estimates have been revised by updating the estimated lifetime of electrical equipment and the estimated historical emission rate during equipment manufacturing. Previously, it was assumed that the equipment lifetime was 30 years, and that during manufacture 22.5 percent of the SF₆ purchased by equipment manufacturers was emitted. These variables have been revised to 40 years and 18.8 percent, respectively, to reflect new data presented in IPCC *Guidelines for National Greenhouse Gas Inventories* (IPCC 2006). Based on these revisions, SF₆ emissions from electric transmission and distribution have decreased by approximately 1 percent for each year during the 1999 to 2004 period. Between 1990 and 1998, estimates have changed between -16 percent (decrease) to +5 percent (increase) depending on the specific year, relative to the previous report.

4.20. Semiconductor Manufacture (IPCC Source Category 2F6)

The semiconductor industry uses multiple long-lived fluorinated gases in plasma etching and plasma enhanced chemical vapor deposition (PECVD) processes to produce semiconductor products. The gases most commonly employed are trifluoromethane (HFC-23 or CHF₃), perfluoromethane (CF₄), perfluoroethane (C₂F₆), nitrogen trifluoride (NF₃), and sulfur hexafluoride (SF₆), although other compounds such as perfluoropropane (C₃F₈) and perfluorocyclobutane (c-C₄F₈) are also used. The exact combination of compounds is specific to the process employed.

A single 300 mm silicon wafer that yields between 400 to 500 semiconductor products (devices or chips) may require as many as 100 distinct fluorinated-gas-using process steps, principally to deposit and pattern dielectric films. Plasma etching (or patterning) of dielectric films, such as silicon dioxide and silicon nitride, is performed to

provide pathways for conducting material to connect individual circuit components in each device. The patterning process uses plasma-generated fluorine atoms, which chemically react with exposed dielectric film, to selectively remove the desired portions of the film. The material removed as well as undissociated fluorinated gases flow into waste streams and, unless emission abatement systems are employed, into the atmosphere. PECVD chambers, used for depositing dielectric films, are cleaned periodically using fluorinated and other gases. During the cleaning cycle the gas is converted to fluorine atoms in plasma, which etches away residual material from chamber walls, electrodes, and chamber hardware. Undissociated fluorinated gases and other products pass from the chamber to waste streams and, unless abatement systems are employed, into the atmosphere. In addition to emissions of unreacted gases, some fluorinated compounds can also be transformed in the plasma processes into different fluorinated compounds which are then exhausted, unless abated, into the atmosphere. For example, when C_2F_6 is used in cleaning or etching, CF_4 is generated and emitted as a process by-product. Besides dielectric film etching and PECVD chamber cleaning, much smaller quantities of fluorinated gases are used to etch polysilicon films and refractory metal films like tungsten.

For 2005, total weighted emissions of all fluorinated greenhouse gases by the U.S. semiconductor industry were estimated to be 4.3 Tg CO_2 Eq. Combined emissions of all fluorinated greenhouse gases are presented in Table 4-73 and Table 4-74, below. The rapid growth of this industry and the increasing complexity (growing number of layers) of semiconductor products led to an increase in emissions of 147 percent between 1990 and 1999. The emissions growth rate began to slow after 1997, and emissions declined by 41 percent between 1999 and 2005. The initial implementation of PFC emission reduction methods such as process optimization and abatement technologies is responsible for this decline. Together, these two trends resulted in a net increase in emissions of 47 percent between 1990 and 2005.

Table 4-73: PFC, HFC, and SF_6 Emissions from Semiconductor Manufacture (Tg CO_2 Eq.)

Year	1990	1995	2000	2001	2002	2003	2004	2005
CF_4	0.7	1.3	1.8	1.3	1.1	1.0	1.2	1.1
C_2F_6	1.5	2.5	3.0	2.1	2.2	2.1	2.2	1.9
C_3F_8	0.0	+	0.1	0.1	0.1	0.1	0.0	0.0
C_4F_8	0.0	+	0.0	0.0	0.0	0.1	0.1	0.1
HFC-23	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2
SF_6	0.5	0.9	1.1	0.8	0.7	0.8	0.9	1.0
NF_3^*	0.0	0.1	0.1	0.1	0.3	0.2	0.3	0.2
Total	2.9	5.0	6.3	4.5	4.4	4.3	4.7	4.3

Note: Totals may not sum due to independent rounding.

* NF_3 emissions are presented for informational purposes, using a GWP of 8,000, and are not included in totals.

Table 4-74: PFC, HFC, and SF_6 Emissions from Semiconductor Manufacture (Mg)

Year	1990	1995	2000	2001	2002	2003	2004	2005
CF_4	115	192	281	202	175	161	185	163
C_2F_6	160	272	324	231	244	228	245	211
C_3F_8	0	0	17	14	9	13	6	4
C_4F_8	0	0	0	0	5	8	9	13
HFC-23	15	26	23	16	15	17	20	18
SF_6	22	38	46	31	28	35	38	40
NF_3	3	6	11	12	32	30	31	27

Methodology

Emissions from semiconductor manufacturing were estimated using three distinct methods, one each for the periods 1990 through 1994, 1995 through 1999, and 2000 and beyond. For 1990 through 1994, emissions were estimated

using the most recent version of EPA's PFC Emissions Vintage Model (PEVM) (Burton and Beizaie 2001).¹⁵ PFC emissions per square centimeter of silicon increase as the number of layers in semiconductor devices increases. Thus, PEVM incorporates information on the two attributes of semiconductor devices that affect the number of layers: (1) linewidth technology (the smallest feature size, which leads to an increasing number of layers),¹⁶ and (2) product type (memory vs. logic).¹⁷ PEVM derives historical consumption of silicon (i.e., square centimeters) by linewidth technology from published data on annual wafer starts and average wafer size (Burton and Beizaie 2001). For each linewidth technology, a weighted average number of layers is estimated using VLSI product-specific worldwide silicon demand data in conjunction with complexity factors (i.e., the number of layers per IC) specific to product type (Burton and Beizaie 2001, ITRS 2005). The distribution of memory/logic devices ranges over the period covered from 52 percent logic devices in 1995 to 59 percent logic devices in 2000. These figures were used to determine emission factors that express emissions per average layer per unit of area of silicon consumed during product manufacture. The per-layer emission factor was based on the total annual emissions reported by participants in EPA's PFC Reduction/Climate Partnership for the Semiconductor Industry in 1995 and later years.

For 1995 through 1999, total U.S. emissions were extrapolated from the total annual emissions reported by the Partnership participants (2005 Aggregate PFC Emissions provided to EPA by Latham & Watkins). The emissions reported by the participants were divided by the ratio of the total layer-weighted capacity of the plants operated by the participants and the total layer-weighted capacity of all of the semiconductor plants in the United States; this ratio represents the share of layer-weighted capacity attributable to partnership participants. The layer-weighted capacity of a plant (or group of plants) consists of the silicon capacity of that plant multiplied by the estimated number of layers used to fabricate products at that plant. This method assumes that participants and non-participants have similar capacity utilizations and per-layer emission factors. Plant capacity, linewidth technology, products manufactured information is contained in the World Fab Watch (WFW) database, which is updated quarterly (see for example, Semiconductor Equipment and Materials Industry 2006).

The U.S. estimate for the years 2000 through 2005—the period during which partners began the consequential application of PFC-reduction measures—was based on a different estimation method. The emissions reported by Partnership participants for each year were accepted as the quantity emitted from the share of the industry represented by those Partners. Remaining emissions (those from non-partners), however, were estimated using PEVM and the method described above. (Non-partners are assumed not to have implemented any PFC-reduction measures, and PEVM models emissions without such measures.) The portion of the U.S. total attributed to non-Partners is obtained by multiplying PEVM's total U.S. figure by the non-partner share of total layer-weighted silicon capacity for each year (as described above). Annual updates to PEVM reflect published figures for actual silicon consumption from VLSI Research, Inc. as well as revisions and additions to the world population of semiconductor manufacturing plants (see Semiconductor Equipment and Materials Industry 2006).^{18,19}

¹⁵ The most recent version of this model is v.3.2.0506.0507, completed in September 2005.

¹⁶ By decreasing features of IC components, more components can be manufactured per device, which increases its functionality. However, as those individual components shrink it requires more layers to interconnect them to achieve the functionality. For example, a microprocessor manufactured with the smallest feature sizes (65 nm) might contain as many as 1 billion transistors and requires as many as 11 layers of component interconnects to achieve functionality while a device manufactured with 130 nm feature size might contain a few hundred million transistors and require 8 layers of component interconnects (ITRS, 2005).

¹⁷ Memory devices manufactured with the same feature sizes as microprocessors (a logic device) require approximately one-half the number of interconnect layers (ITRS, 2005).

¹⁸ Special attention was given to the manufacturing capacity of plants that use wafers with 300 mm diameters because the actual capacity of these plants in 2004 is below design capacity, the figure provided in WFW. To prevent overstating estimates of partner-capacity shares from plants using 300 mm wafers, *design* capacities contained in WFW were replaced with estimates of *actual installed* capacities for 2004 published by Citigroup Smith Barney (2005). Without this correction, the partner share of capacity would be overstated, by approximately 5 percentage points. For perspective, approximately 95 percent of all new capacity additions in 2004 used 300 mm wafers and by year-end those plants, on average, could operate at but approximately 70 percent of the design capacity. For 2005, actual installed capacities was estimated using an entry in the World Fab Watch

Two different approaches were also used to estimate the distribution of emissions of specific PFCs. Before 1999, when there was no consequential adoption of PFC-reducing measures, a fixed distribution was assumed to apply to the entire U.S. industry. This distribution was based upon the average PFC purchases by semiconductor manufacturers during this period and the application of IPCC default emission factors for each gas (Burton and Beizaie 2001). For the 2000 through 2005 period, the 1990 through 1999 distribution was assumed to apply to the non-Partners. Partners, however, began to report gas-specific emissions during this period. Thus, gas specific emissions for 2000 through 2005 were estimated by adding the emissions reported by the Partners to those estimated for the non-Partners.²⁰

Partners estimate their emissions using a range of methods. For 2005, we assume that most partners used a method as least as accurate as the IPCC's Tier 2c Methodology, recommended in the IPCC (2000), since that has been their approach for the past several years. However, this is expected to change with publication of the updated IPCC (2006). The partners with relatively high emissions typically use the more accurate IPCC 2b or 2a methods, multiplying estimates of their PFC consumption by process-specific emission factors that they have either measured or obtained from tool suppliers.

Data used to develop emission estimates were prepared in cooperation with the Partnership. Estimates of operating plant capacities and characteristics for participants and non-participants were derived from the Semiconductor Equipment and Materials Industry (SEMI) *World Fab Watch* (formerly *International Fabs on Disk*) database (1996 to 2006). Estimates of silicon consumed by line-width from 1990 through 2005 were derived from information from VLSI Research (2005), and the number of layers per line-width was obtained from International Technology Roadmap for Semiconductors: 1998-2004 (Burton and Beizaie 2001, ITRS 2005).

Uncertainty

A quantitative uncertainty analysis of this source category was performed using the IPCC-recommended Tier 2 uncertainty estimation methodology, the Monte Carlo Stochastic Simulation technique. The equation used to estimate uncertainty is:

$$\text{U.S. emissions} = \text{PEVM estimate} - (\text{Partnership share} * \text{PEVM estimate}) + \text{Partnership submittal}$$

The Monte Carlo analysis results presented below relied on estimates of uncertainty attributed to the three variables on the right side of the equation. Estimates of uncertainty for the three variables were in turn developed using the estimated uncertainties associated with the individual inputs to each variable, error propagation analysis, and expert judgment. For the relative uncertainty associated with the PEVM estimate in 2005, an uncertainty of ± 20 percent was estimated, using the calculus of error propagation and considering the aggregate average emission factor, world silicon consumption, and the U.S. share of layer-weighted silicon capacity. For the share of U.S. layer-weighted silicon capacity accounted for by Partners, a relative uncertainty of ± 10 percent was estimated based on information from the firm that compiled the *World Fab Watch* database (SMA 2003). For the aggregate PFC emissions data supplied to the partnership, a relative uncertainty of approximately ± 10 percent was estimated (representing a 95 percent confidence interval).

database (April 2006 Edition) called "wafers/month, 8-inch equivalent, which denotes the actual installed capacity instead of the fully-ramped capacity.

¹⁹ In 2005, the trend in co-ownership of manufacturing facilities in the industry continued. Several manufacturers, who are partners, now operate fabs with other manufacturers, who in some cases are also partners and in other cases not partners. Special attention was given to this occurrence when estimating the partner and non-partner shares of US layer-weighted manufacturing capacity.

²⁰ In recent years, the Partnership started reporting gas-specific emissions using GWP values from the Third Assessment Report (TAR), while in previous years the values were taken from the Second Assessment Report (SAR). The emissions reported here are restated using GWPs from the SAR.

Consideration was also given to the nature and magnitude of the potential bias that PEVM might have in its estimates of the number of layers associated with devices manufactured at each technology node. The result of a brief analysis indicated that PEVM overstates the average number of layers across all product categories and all manufacturing technologies for 2004 by 0.12 layers or 2.9 percent. This bias is represented in the uncertainty analysis by deducting the absolute bias value from the PEVM emission estimate when it is incorporated into the Monte Carlo analysis.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-75. The emissions estimate for total U.S. PFC emissions from semiconductor manufacturing were estimated to be between 3.6 and 5.4 Tg CO₂ Eq. at a 95 percent confidence level. This range represents 21 percent below to 20 percent above the 2005 emission estimate of 4.5 Tg CO₂ Eq. This range and the associated percentages apply to the estimate of total emissions rather than those of individual gases. Uncertainties associated with individual gases will be somewhat higher than the aggregate, but were not explicitly modeled.

Table 4-75: Tier 2 Quantitative Uncertainty Estimates for HFC, PFC, and SF₆ Emissions from Semiconductor Manufacture (Tg CO₂ Eq. and Percent)

Manufacture (Tg CO ₂ Eq. and Percent)						
Source	Gas	2005	Uncertainty Range			
		Emission	Relative to Emission Estimate ^b			
		Estimate ^a	(Tg CO ₂ Eq.)			
		(Tg CO ₂ Eq.)	(Tg CO ₂ Eq.)	(%)		
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Semiconductor Manufacture	HFC, PFC, and SF ₆	4.3	3.6	5.4	-21%	+20%

^a Because the uncertainty analysis covered all emissions (including NF₃), the emission estimate presented here does not match that shown in Table 4-73.

^b Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Planned Improvements

The method to estimate non-partner related emissions (i.e., PEVM) is not expected to change (with the exception of possible future updates to emission factors and added technology nodes). Future improvements to the national emission estimates will primarily be associated with determining the portion of national emissions to attribute to partner report totals (about 80 percent in recent years). As the nature of the partner reports change through time and industry-wide reduction efforts increase, consideration will be given to what emission reduction efforts—if any—are likely to be occurring at non-partner facilities. (Currently none are assumed to occur.)

4.21. Aluminum Production (IPCC Source Category 2C3)

Aluminum is a light-weight, malleable, and corrosion-resistant metal that is used in many manufactured products, including aircraft, automobiles, bicycles, and kitchen utensils. In 2005, the United States was the fourth largest producer of primary aluminum, with approximately eight percent of the world total (USGS 2006). The United States was also a major importer of primary aluminum. The production of primary aluminum—in addition to consuming large quantities of electricity—results in process-related emissions of CO₂ and two perfluorocarbons (PFCs): perfluoromethane (CF₄) and perfluoroethane (C₂F₆).

CO₂ is emitted during the aluminum smelting process when alumina (aluminum oxide, Al₂O₃) is reduced to aluminum using the Hall-Heroult reduction process. The reduction of the alumina occurs through electrolysis in a molten bath of natural or synthetic cryolite (Na₃AlF₆). The reduction cells contain a C lining that serves as the cathode. C is also contained in the anode, which can be a C mass of paste, coke briquettes, or prebaked C blocks from petroleum coke. During reduction, most of this C is oxidized and released to the atmosphere as CO₂.

Process emissions of CO₂ from aluminum production were estimated to be 4.2 Tg CO₂ Eq. (4,208 Gg) in 2005 (see Table 4-76). The C anodes consumed during aluminum production consist of petroleum coke and, to a minor

extent, coal tar pitch. The petroleum coke portion of the total CO₂ process emissions from aluminum production is considered to be a non-energy use of petroleum coke, and is accounted for here and not under the CO₂ from Fossil Fuel Combustion source category of the Energy sector. Similarly, the coal tar pitch portion of these CO₂ process emissions is accounted for here rather than in the Iron and Steel source category of the Industrial Processes sector.

Table 4-76: CO₂ Emissions from Aluminum Production (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	6.8	6,831
1995	5.7	5,659
2000	6.1	6,086
2001	4.4	4,381
2002	4.5	4,490
2003	4.5	4,503
2004	4.2	4,231
2005	4.2	4,208

In addition to CO₂ emissions, the aluminum production industry is also a source of PFC emissions. During the smelting process, when the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, which are termed “anode effects.” These anode effects cause C from the anode and fluorine from the dissociated molten cryolite bath to combine, thereby producing fugitive emissions of CF₄ and C₂F₆. In general, the magnitude of emissions for a given level of production depends on the frequency and duration of these anode effects. As the frequency and duration of the anode effects increase, emissions increase.

Since 1990, emissions of CF₄ and C₂F₆ have both declined by 84 percent to 2.5 Tg CO₂ Eq. of CF₄ (0.4 Gg) and 0.4 Tg CO₂ Eq. of C₂F₆ (0.05 Gg) in 2005, as shown in Table 4-77 and Table 4-78. This decline is due both to reductions in domestic aluminum production and to actions taken by aluminum smelting companies to reduce the frequency and duration of anode effects. Since 1990, aluminum production has declined by 39 percent, while the average CF₄ and C₂F₆ emission rates (per metric ton of aluminum produced) have each been reduced by 74 percent.

Table 4-77: PFC Emissions from Aluminum Production (Tg CO₂ Eq.)

Year	CF ₄	C ₂ F ₆	Total
1990	15.9	2.7	18.5
1995	10.2	1.7	11.8
2000	7.8	0.8	8.6
2001	3.0	0.4	3.5
2002	4.6	0.7	5.2
2003	3.3	0.5	3.8
2004	2.4	0.4	2.8
2005	2.5	0.4	3.0

Note: Totals may not sum due to independent rounding.

Table 4-78: PFC Emissions from Aluminum Production (Gg)

Year	CF ₄	C ₂ F ₆
1990	2.4	0.3
1995	1.6	0.2
2000	1.2	0.1
2001	0.5	+
2002	0.7	0.1

2003	0.5	0.1
2004	0.4	+
2005	0.4	+

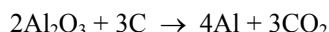
+ Does not exceed 0.05 Gg

In 2005, U.S. primary aluminum production totaled approximately 2.5 million metric tons, similar to 2004 production levels. Due to high electric power costs in various regions of the country, aluminum production has been curtailed at several U.S. smelters, which resulted in 2005 production levels that were approximately 34 percent lower than the levels in 1999, the year with the highest production over the prior decade, 1995 through 2005. The transportation industry remained the largest domestic consumer of primary aluminum, accounting for about 39 percent of U.S. consumption (USGS 2006).

Methodology

CO₂ emissions released during aluminum production were estimated using the combined application of process-specific emissions estimates modeling with individual partner reported data. These estimates are achieved through information gathered by EPA's Voluntary Aluminum Industrial Partnership (VAIP) program.

Most of the CO₂ emissions released during aluminum production occur during the electrolysis reaction of the C anode, as described by the following reaction.



For prebake smelter technologies, CO₂ is also emitted during the anode baking process. These emissions can account for approximately 10 percent of total process CO₂ emissions from prebake smelters. The CO₂ emission factor employed was estimated from the production of primary aluminum metal and the C consumed by the process. Emissions vary depending on the specific technology used by each plant (e.g., prebake or Söderberg). CO₂ process emissions were estimated using the methodology recommended by IPCC (2006).

The prebake process specific formula recommended by IPCC (2006) accounts for various parameters, including net C consumption, and the sulfur, ash, and impurity content of the baked anode. For anode baking emissions, process formulas account for packing coke consumption, the sulfur and ash content of the packing coke, as well as the pitch content and weight of baked anodes produced. The Söderberg process formula accounts for the weight of paste consumed per metric ton of aluminum produced, and pitch properties, including sulfur, hydrogen, and ash content.

Through the VAIP, process data have been reported for 1990, 2000, 2003, 2004, and 2005. Where available, smelter-specific process data reported under the VAIP were used; however, if the data were incomplete or unavailable, information was supplemented using industry average values recommended by IPCC (2006). Smelter-specific CO₂ process data were provided by 18 of the 23 operating smelters in 1990 and 2000, by 14 out of 16 operating smelters in 2003 and 2004, and by 14 out of 15 operating smelters in 2005. For years where CO₂ process data were not reported by these companies, estimates were developed through linear interpolation, and/or assuming industry default values.

In the absence of any smelter specific process data (i.e., 1 out of 15 smelters in 2005, and 5 out of 23 between 1990 and 2003), CO₂ emission estimates were estimated using Tier 1 Söderberg and/or Prebake emission factors (metric ton of CO₂ per metric ton of aluminum produced) from IPCC(2006)

Aluminum production data for all operating smelters were reported under the VAIP in 2005. Between 1990 and 2004, production data were provided by 21 of the 23 U.S. smelters that operated during at least part of that period. For the non-reporting smelters, production was estimated based on the difference between reporting smelters and national aluminum production levels (USAA 2006), with allocation to specific smelters based on reported production capacities (USGS 2002).

PFC emissions from aluminum production were estimated using a per-unit production emission factor that is expressed as a function of operating parameters (anode effect frequency and duration), as follows:

$$\text{PFC (CF}_4 \text{ or C}_2\text{F}_6\text{) kg/metric ton Al} = S \times \text{Anode Effect Minutes/Cell-Day}$$

where,

S = Slope coefficient (kg PFC/metric ton Al/(Anode Effect minutes/cell day))

Anode Effect Minutes/Cell-Day = Anode Effect Frequency/Cell-Day \times Anode Effect Duration (minutes)

Smelter-specific slope coefficients that are based on field measurements yield the most accurate results. To estimate emissions between 1990 and 2004, smelter-specific coefficients were available and were used for 12 out of the 23 U.S. smelters that operated during at least part of that period. To estimate 2005 emissions, smelter-specific coefficients were available and were used for 5 out of the 15 operating U.S. smelters, representing approximately 33 percent of operating 2005 U.S. production capacity. For the remaining 10 operating smelters, technology-specific slope coefficients from IPCC (2001) were applied. The slope coefficients were combined with smelter-specific anode effect data collected by aluminum companies and reported under the VAIP, to estimate emission factors over time. In 2005, smelter-specific anode effect data were available for all operating smelters. Where smelter-specific anode effect data were not available (i.e., 2 out of 23 smelters between 1990 and 2004), industry averages were used. For all smelters, emission factors were multiplied by annual production to estimate annual emissions at the smelter level. In 2005, smelter-specific production data were available for all operating smelters. Between 1990 and 2004, production data has been provided by 21 of the 23 U.S. smelters. Emissions were then aggregated across smelters to estimate national emissions. The methodology used to estimate emissions is consistent with the methodologies recommended by IPCC (2006).

National primary aluminum production data for 1990 through 2001 (see Table 4-79) were obtained from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1995, 1998, 2000, 2001, 2002). For 2002 through 2005, national aluminum production data were obtained from the United States Aluminum Association's *Primary Aluminum Statistics* (USAA 2004, 2005, 2006).

Table 4-79: Production of Primary Aluminum (Gg)

Year	Gg
1990	4,048
1995	3,375
2000	3,668
2001	2,637
2002	2,705
2003	2,705
2004	2,517
2005	2,478

Uncertainty

The overall uncertainties associated with the 2005 CO₂, CF₄, and C₂F₆ emission estimates were calculated using Approach 2, as defined by IPCC (2006). For CO₂, uncertainty was assigned to each of the parameters used to estimate CO₂ emissions. Uncertainty surrounding reported production data was assumed to be 2 percent (IPCC 2006). For additional variables, such as net C consumption, and sulfur and ash content in baked anodes, estimates for uncertainties associated with reported and default data were obtained from IPCC (2006). A Monte Carlo analysis was applied to estimate the overall uncertainty of the CO₂ emission estimate for the U.S. aluminum industry as a whole, and the results are provided below.

To estimate the uncertainty associated with emissions of CF₄ and C₂F₆, the uncertainties associated with three variables were estimated for each smelter: (1) the quantity of aluminum produced, (2) the anode effect minutes per cell day (which may be reported directly or calculated as the product of anode effect frequency and anode effect duration), and (3) the smelter- or technology-specific slope coefficient. A Monte Carlo analysis was then applied to estimate the overall uncertainty of the emission estimate for each smelter or company and for the U.S. aluminum

industry as a whole.

The results of this quantitative uncertainty analysis are summarized in Table 4-80. Aluminum production-related CO₂ emissions were estimated to be between 4.0 and 4.4 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 5 percent below to 5 percent above the emission estimate of 4.2 Tg CO₂ Eq. Also, production-related CF₄ emissions were estimated to be between 2.3 and 2.7 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 8 percent below to 8 percent above the emission estimate of 2.5 Tg CO₂ Eq. Finally, aluminum production-related C₂F₆ emissions were estimated to be between 0.4 and 0.5 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 15 percent below to 16 percent above the emission estimate of 0.4 Tg CO₂ Eq.

Table 4-80: Tier 2 Quantitative Uncertainty Estimates for CO₂ and PFC Emissions from Aluminum Production (Tg CO₂ Eq. and Percent)

Source	Gas	2005	Uncertainty Range Relative to 2005 Emission Estimate ^a			
		Emission	(Tg CO ₂ Eq.)		(%)	
		Estimate	Lower	Upper	Lower	Upper
		(Tg CO ₂ Eq.)	Bound	Bound	Bound	Bound
Aluminum Production	CO ₂	4.2	4.0	4.4	-5%	+5%
Aluminum Production	CF ₄	2.5	2.3	2.7	-8%	+8%
Aluminum Production	C ₂ F ₆	0.4	0.4	0.5	-15%	+16%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Note that the 2005 emission estimate was developed using IPCC (2001) slope coefficients for the 10 operating smelters without site-specific PFC measurements. If these slope coefficients were revised to incorporate recent IPCC (2006) slope data, overall PFC emission estimates for 2005 would be on the order of 10 percent lower than current estimates. Additionally, since these smelters are owned by one company, data have been reported on a company-wide basis as totals or weighted averages. Consequently, uncertainties in anode effect minutes per cell day, slope coefficients, and aluminum production have been applied to the company as a whole, and not on a smelter-specific basis. This probably overestimates the uncertainty associated with the cumulative emissions from these smelters, because errors that were in fact independent were treated as if they were correlated. It is therefore likely that uncertainties calculated above for the total U.S. 2005 emission estimates for CF₄ and C₂F₆ are also high.

This inventory may slightly underestimate greenhouse gas emissions from aluminum production and casting because it does not account for the possible use of SF₆ as a cover gas or a fluxing and degassing agent in experimental and specialized casting operations. The extent of such use in the U.S. is not known. Historically, SF₆ emissions from aluminum activities have been omitted from estimates of global SF₆ emissions, with the explanation that any emissions would be insignificant (Ko et al. 1993, Victor and MacDonald 1998). The concentration of SF₆ in the mixtures is small and a portion of the SF₆ is decomposed in the process (MacNeal et al. 1990, Garipey and Dube 1992, Ko et al. 1993, Ten Eyck and Lukens 1996, Zurecki 1996).

Recalculations Discussion

Relative to the previous Inventory report, CO₂ emission estimates for the period 1990 through 2004 were updated based on revisions to default parameters used in the estimation methodology. Previous CO₂ emission estimates were based on default emission factors defined by IPCC/UNEP/OED/IEA (1997) and *Aluminum Sector Greenhouse Gas Protocol* (IAI 2003). Current estimates utilize default parameters defined in IPCC (2006). Based on this revision, CO₂ emissions from aluminum production have decreased by approximately 3 percent for each year during the 1990 to 2004 period relative to the previous report.

The default slope coefficients used to estimate PFC emissions from two smelters that have not developed Tier 3b site-specific estimates were revised to reflect data presented in IPCC (2006). This change has resulted in an increase in PFC emissions of approximately 1 percent in 1990, an average decrease of 0.1 percent between 1991 and 1996 and 2002 through 2004, and an average decrease of 6 percent from 1997 through 2001, relative to the estimates developed for the 1990 to 2004 inventory.

4.22. Magnesium Production and Processing (IPCC Source Category 2C4)

The magnesium metal production and casting industry uses sulfur hexafluoride (SF₆) as a cover gas to prevent the rapid oxidation of molten magnesium in the presence of air. A dilute gaseous mixture of SF₆ with dry air and/or CO₂ is blown over molten magnesium metal to induce and stabilize the formation of a protective crust. A small portion of the SF₆ reacts with the magnesium to form a thin molecular film of mostly magnesium oxide and magnesium fluoride. The amount of SF₆ reacting in magnesium production and processing is assumed to be negligible and thus all SF₆ used is assumed to be emitted into the atmosphere. Sulfur hexafluoride has been used in this application around the world for the last twenty years.

The magnesium industry emitted 2.7 Tg CO₂ Eq. (0.1 Gg) of SF₆ in 2005, representing an increase of approximately 2 percent from 2004 emissions (see Table 4-81). A planned expansion of primary magnesium production in the United States has been delayed due to unfavorable market conditions. Antidumping duties imposed on Chinese imports by the U.S. International Trade Commission have shifted the majority of U.S. demand for primary magnesium to imports from Canada, Israel, and Russia (USGS 2006). Die casting operations in the United States have remained stable and are expected to increase as demand for die cast parts for the automotive sector increases due to fuel efficiency design objectives.

Table 4-81: SF₆ Emissions from Magnesium Production and Processing (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	5.4	0.2
1995	5.6	0.2
2000	3.0	0.1
2001	2.4	0.1
2002	2.4	0.1
2003	2.9	0.1
2004	2.6	0.1
2005	2.7	0.1

Methodology

1999 to 2005 Emissions

Emission estimates for the magnesium industry from 1999 through 2005 incorporate information provided by industry participants in EPA's SF₆ Emission Reduction Partnership for the Magnesium Industry. The Partnership started in 1999 and currently, participating companies represent 100 percent of U.S. primary and secondary production and 90 percent of the casting sector (i.e., die, sand, permanent mold, wrought, and anode casting). Absolute emissions for 1999 through 2005 from primary production, secondary production (i.e., recycling), and die casting were reported by Partnership participants. Emission factors for 2002 to 2005 for sand casting activities were also acquired through the Partnership. The 1999 through 2005 emissions from casting operations (other than die) were estimated by multiplying emission factors (kg SF₆ per metric ton of Mg produced or processed) by the amount of metal produced or consumed. U.S. magnesium metal production (primary and secondary) and consumption (casting) data from 1990 through 2005 were available from the USGS (USGS 2002, 2003, 2005a, 2005b, 2006). The emission factors for casting activities are provided below in Table 4-82. The emission factors for primary production, secondary production, and sand casting are withheld to protect company-specific production information. However, the emission factor for primary production has not risen above the 1995 value of 1.1 kg SF₆ per metric ton, and the emission factor for secondary production is slightly lower than the industry-reported historic value of 1 kg SF₆ per metric ton.

Die casting emissions for 1999 through 2005, which accounted for 33 to 52 percent of all SF₆ emissions from the U.S. magnesium industry during this period, were estimated based on information supplied by industry Partners. From 2000 to 2005, Partners accounted for all U.S. die casting that was tracked by USGS. If Partners did not report

emissions data for a certain year, SF₆ emissions data were estimated using available information on emission factors and production reported in prior years. Each non-reporting Partner's production was assumed to have remained constant since the last report, while each non-reporting Partner's emission factor was assumed to have followed the same trend as the emission factors for reporting die casting partners. Emissions from non-reporting Partners are estimated to have accounted for less than 15 percent of die-casting emissions in all years since 1999.

In 1999, Partners did not account for all die casting tracked by USGS, and, therefore, it was necessary to estimate the emissions of die casters who were not Partners. Die casters who were not Partners were assumed to be similar to Partners who cast small parts. Due to process requirements, these casters consume larger quantities of SF₆ per metric ton of processed magnesium than casters that process large parts. Consequently, emission estimates from this group of die casters were developed using an average emission factor of 5.2 kg SF₆ per metric ton of magnesium. The emission factors for the other industry sectors (i.e., permanent mold, wrought, and anode casting) were based on discussions with industry representatives.

Table 4-82: SF₆ Emission Factors (kg SF₆ per metric ton of magnesium)

Year	Permanent			
	Die Casting	Mold	Wrought	Anodes
1999	2.14 ^a	2	1	1
2000	0.73	2	1	1
2001	0.77	2	1	1
2002	0.70	2	1	1
2003	0.84	2	1	1
2004	0.78	2	1	1
2005	0.75	2	1	1

^a Weighted average that includes an estimated emission factor of 5.2 kg SF₆ per metric ton of magnesium for die casters that do not participate in the Partnership.

1990 to 1998 Emissions

To estimate emissions for 1990 through 1998, industry emission factors were multiplied by the corresponding metal production and consumption (casting) statistics from USGS. The primary production emission factors were 1.2 kg per metric ton for 1990 through 1993, and 1.1 kg per metric ton for 1994 through 1996. These factors were based on information reported by U.S. primary producers. For die casting, an emission factor of 4.1 kg per metric ton was used for the period 1990 through 1996, based on an international survey (Gjestland & Magers 1996). For 1996 through 1998, the emission factors for primary production and die casting were assumed to decline linearly to the level estimated based on Partner reports in 1999. This assumption is consistent with the trend in SF₆ sales to the magnesium sector that is reported in the RAND survey of major SF₆ manufacturers, which shows a decline of 70 percent from 1996 to 1999 (RAND 2002). The emission factor for sand casting between 1990 and 2001 was assumed to have been the same as the 2002 emission factor provided by Partners for this process. The emission factor for secondary production from 1990 through 1998 was similarly assumed to be constant at 1 kg per metric ton. The emission factors for the other processes (i.e., permanent mold, wrought, and anode casting), about which less is known, were assumed to remain constant at levels defined in Table 4-82.

Uncertainty

To estimate the uncertainty of the estimated 2005 SF₆ emissions from magnesium production and processing, the uncertainties associated with three variables were estimated: (1) emissions reported by magnesium producers and processors that participate in the Partnership, (2) emissions estimated for magnesium producers and processors that participate in the Partnership but did not report this year, and (3) emissions estimated for magnesium producers and processors that do not participate in the Partnership. In general, where precise quantitative information was not available on the uncertainty of a parameter, an upper-bound value was used.

Additional uncertainties exist in these estimates, such as the basic assumption that SF₆ neither reacts nor decomposes during use. The melt surface reactions and high temperatures associated with molten magnesium could potentially cause some gas degradation. Recent measurement studies have identified SF₆ cover gas degradation at hot-chambered die casting machines on the order of 10 percent (Bartos et al. 2003). As is the case for other sources

of SF₆ emissions, total SF₆ consumption data for magnesium production and processing in the United States were not available. Sulfur hexafluoride may also be used as a cover gas for the casting of molten aluminum with high magnesium content; however, to what extent this technique is used in the United States is unknown.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-83. SF₆ emissions associated with magnesium production and processing were estimated to be between 2.6 and 2.8 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 4 percent below to 4 percent above the 2005 emissions estimate of 2.7 Tg CO₂ Eq.

Table 4-83: Tier 2 Quantitative Uncertainty Estimates for SF₆ Emissions from Magnesium Production and Processing (Tg CO₂ Eq. and Percent)

Source	Gas	2005 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Magnesium Production	SF ₆	2.7	2.6	2.8	-4%	+4%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

The methodology for estimating secondary magnesium production (recycling) emissions from 1999 to 2005 was adjusted to rely solely on Partner-reported information, because this was believed to yield a more accurate estimate than adding Partner-reported emissions to the product of USGS secondary magnesium production and a default industry SF₆ emission factor. In previous years, the “remelt” activity reported by Partners was small compared to the secondary production reported by USGS, and it was uncertain whether this remelt activity was included in USGS totals. Thus, emissions were estimated both for Partner-reported remelt and for USGS-reported secondary production. With the addition of new Partners, however, it appears that Partner-reported remelt is actually a more complete estimate of U.S. secondary production than the USGS value. Thus, to avoid double-counting, only the emissions reported by the Partners are included in the totals for the time series. The change resulted in a decrease of 0.2 Tg CO₂ Eq. (approximately 7 percent) in SF₆ emissions from magnesium production and processing for 1999 to 2002, and a decrease in SF₆ emissions of 0.1 Tg CO₂ Eq. (approximately 4 percent) for 2003 to 2004 relative to the previous report.

Planned Improvements

As more work assessing the degree of cover gas degradation and associated byproducts is undertaken and published, results could potentially be used to refine the emission estimates, which currently assume (per IPCC *Good Practice Guidance*, IPCC 2000) that all SF₆ utilized is emitted to the atmosphere. EPA-funded measurements of SF₆ in hot chamber die casting have indicated that the latter assumption may be incorrect, with observed SF₆ degradation on the order of 10 percent (Bartos et al. 2003). More recent EPA-funded measurement studies have confirmed this observation for cold chamber die casting (EPA 2004). Another issue that will be addressed in future inventories is the likely adoption of alternate cover gases by U.S. magnesium producers and processors. These cover gases, which include AM-Cover™ (containing HFC-134a) and Novec™ 612, have lower GWPs than SF₆, and tend to quickly decompose during their exposure to the molten metal. Additionally, as more companies join the Partnership, in particular those from sectors not currently represented such as permanent mold and anode casting, emission factors will be refined to incorporate these additional data.

4.23. Industrial Sources of Indirect Greenhouse Gases

In addition to the main greenhouse gases addressed above, many industrial processes generate emissions of indirect greenhouse gases. Total emissions of nitrogen oxides (NO_x), carbon monoxide (CO), and non-CH₄ volatile organic compounds (NMVOCs) from non-energy industrial processes from 1990 to 2005 are reported in Table 4-84.

Table 4-84: NO_x, CO, and NMVOC Emissions from Industrial Processes (Gg)

Gas/Source	1990	1995	2000	2001	2002	2003	2004	2005
NO_x	591	607	626	656	532	533	534	535
Other Industrial Processes	343	362	434	457	389	390	390	391
Chemical & Allied Product Manufacturing	152	143	95	97	63	63	63	63
Metals Processing	88	89	81	86	63	63	63	63
Storage and Transport	3	5	14	15	17	17	17	17
Miscellaneous*	5	8	2	1	1	1	1	1
CO	4,125	3,959	2,217	2,339	1,710	1,730	1,751	1,772
Metals Processing	2,395	2,159	1,175	1,252	895	906	917	928
Other Industrial Processes	487	566	538	558	445	450	456	461
Chemical & Allied Product Manufacturing	1,073	1,110	327	338	258	261	264	267
Storage and Transport	69	23	154	162	107	108	109	111
Miscellaneous*	101	102	23	30	5	5	5	4
NMVOCs	2,422	2,642	1,773	1,769	1,811	1,813	1,815	1,818
Storage and Transport	1,352	1,499	1,067	1,082	1,140	1,142	1,143	1,144
Other Industrial Processes	364	408	412	381	400	401	401	402
Chemical & Allied Product Manufacturing	575	599	230	238	227	227	227	227
Metals Processing	111	113	61	65	42	42	42	42
Miscellaneous*	20	23	3	4	2	2	2	2

* Miscellaneous includes the following categories: catastrophic/accidental release, other combustion, health services, cooling towers, and fugitive dust. It does not include agricultural fires or slash/prescribed burning, which are accounted for under the Field Burning of Agricultural Residues source.

Note: Totals may not sum due to independent rounding.

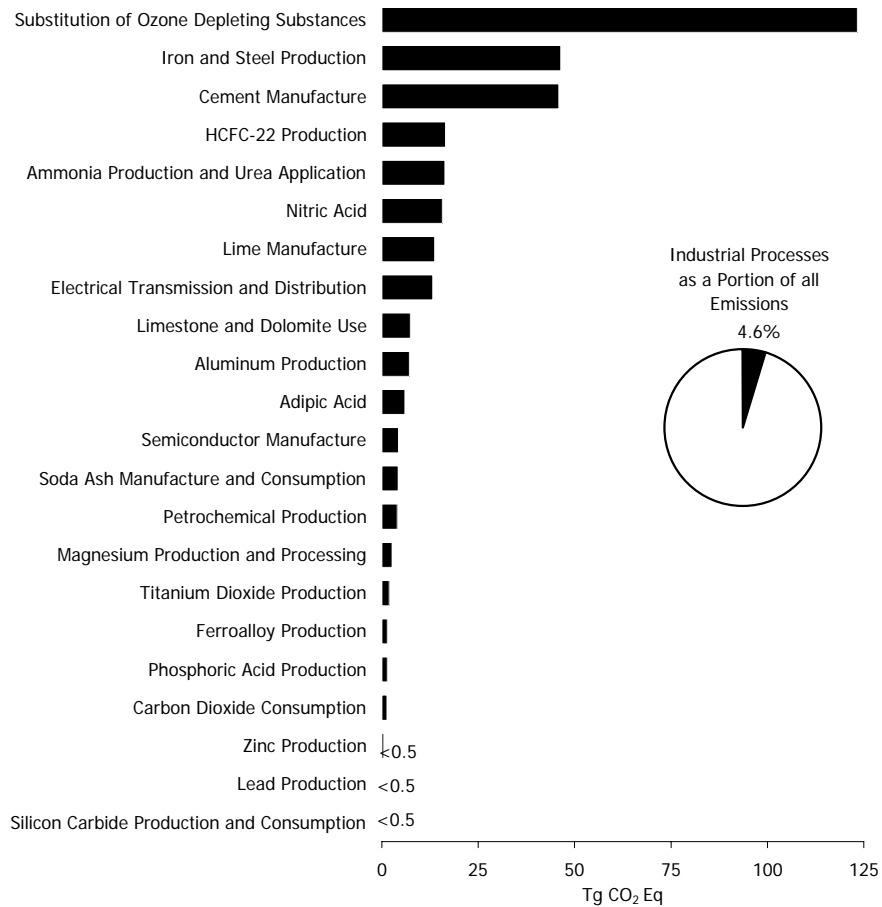
Methodology

These emission estimates were obtained from preliminary data (EPA 2006), and disaggregated based on EPA (2003), which, in its final iteration, will be published on the National Emission Inventory (NEI) Air Pollutant Emission Trends web site. Emissions were calculated either for individual categories or for many categories combined, using basic activity data (e.g., the amount of raw material processed) as an indicator of emissions. National activity data were collected for individual categories from various agencies. Depending on the category, these basic activity data may include data on production, fuel deliveries, raw material processed, etc.

Activity data were used in conjunction with emission factors, which together relate the quantity of emissions to the activity. Emission factors are generally available from the EPA's *Compilation of Air Pollutant Emission Factors, AP-42* (EPA 1997). The EPA currently derives the overall emission control efficiency of a source category from a variety of information sources, including published reports, the 1985 National Acid Precipitation and Assessment Program emissions inventory, and other EPA databases.

Uncertainty

Uncertainties in these estimates are partly due to the accuracy of the emission factors used and accurate estimates of activity data. A quantitative uncertainty analysis was not performed.



n.

Figure 4-1: 2005 Industrial Processes Chapter Greenhouse Gas Sources